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ANALYSIS OF THERMALLY DEGRADED SENSIBLE HEAT STORAGE HYDROCARBONS

V. P. Burolla

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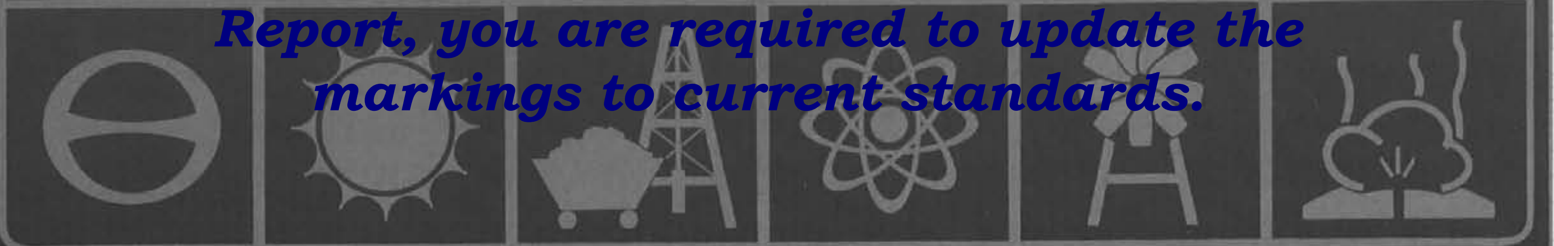

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ABSTRACT

Heat treated samples of three candidate fluids for sensible heat storage were analyzed using gel-permeation chromatography (GPC) and infrared spectrophotometry (IR). Comparison of this data with previous work done at the Rocketdyne Division of Rockwell International reveals that:

a. The oil is undergoing large-scale thermal cracking that is probably catalyzed by the presence of degradation products.

b. The oil is possibly experiencing some amount of dehydrogenation.

c. There is a very small amount of bulk polymerization taking place.

d. There is little reason to suspect that the oils suffered any significant amount of oxidation.

e. The approximate molecular weight range of fresh Caloria HT 43 is from 170 to 550.

Sufficient information is now available to enable design of a processor (fractional distillation column) to ostensibly prolong the usable lifetime of the oil.

Based upon the results of a fairly simplistic test run at Sandia, mechanical shear degradation due to pumping and fluid flow in general should not contribute significantly to fluid decomposition.

ACKNOWLEDGMENT

The contents of this report were prepared with the help of Michael Schalit, Division 8266, and H. Cal Feemster, Division 8313. Their assistance and advice are greatly appreciated.

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ANALYSIS OF THERMALLY DEGRADED SENSIBLE HEAT STORAGE HYDROCARBONS

Introduction

One of the major drawbacks of a solar powered commercial utility is the inability to generate power at night or during low insolation levels. In an attempt to reduce the variations in the power generated and to extend the daily operational period, several schemes have been proposed for storing thermal energy either as latent or sensible heat. Three sensible heat proposals currently being funded by the United States Department of Energy (DOE) include the use of a low-cost oil as the energy storage medium and/or heat transfer medium. Because of the temperatures involved, some concern has been expressed over the usable lifetime of these oils. To identify possible problem areas, a series of tests was conducted (under contract to DOE) at the Rocketdyne Division of Rockwell International,[8] Canoga Park, California, which subjected three candidate hydrocarbon oils to controlled temperatures in a nitrogen atmosphere. Some of the samples were also exposed to granite rock and metal lathe turnings. The scope of the contract only called for measuring and recording the viscosity and weight changes of the oils. A detailed examination of this data indicated that there was not enough information to define exactly what was happening to the oil. For this reason, Sandia Laboratories, Livermore (SLL) personnel performed an analysis using gel-permeation chromatography (GPC) and infrared (IR) spectrophotometry in an attempt to determine the degradation mechanism of the oils. The results of this investigation are reported here. A more detailed description of the tests conducted at Rocketdyne[8] is included in Appendix A, and a complete list of their data may be obtained from Mr. Rex Mitchell.

In addition to the problems described above, some concern was expressed about fluid degradation due to pumping forces and fluid flow conditions in general. In a commercial application, hot fluid would be passed through a centrifugal pump, and therefore, be subject to some amount of mechanical shear. The magnitude of this effect being questionable, an experiment was conducted to determine if any effect could be observed. A schematic diagram and a brief test description are included as Appendix B.

Basis of Analysis

There is sufficient information available in the literature[1,2,3,4] to indicate that both thermal cracking and polymerization would probably occur in any hydrocarbon oil exposed to temperatures typical of the tests and applications previously mentioned. Since GPC had been used successfully by others both for fingerprinting crude oils[5] and analyzing the breakdown of several other classes of organic oils,[6,7] it seemed that it would be the most likely candidate for rapid determinations of thermal cracking and polymerization reactions. In addition, it was necessary to include some analysis capable for detecting chemical changes in the oil that might be affecting the other reactions. For the types of compounds being dealt with, an infrared (IR) analysis seemed most appropriate.

Test Specimen

The heat transfer oils subjected to the thermal tests were Caloria HT 43 marketed by Exxon Company and Therminol 55 and Therminol 66 marketed by Monsanto Company. Caloria HT 43 is reported by the manufacturer to have high temperature capability to 600°F, and Therminol 55 and 66 are reported by the manufacturer to have high temperature capabilities to 550°F and 650°F, respectively. Only Caloria HT 43 was tested for mechanical shear degradation.

Equipment

The chromatographic analysis was accomplished with a Water's Associates liquid chromatograph (ALC 200) equipped with a Model 6000 Solvent Delivery System, a Model 440 UV absorbance detector, and a refractive index (RI) detector. In most of the analyses only two 100 Å microstyragel columns were used; in the remainder, three columns were used--the first being a 500 Å microstyragel and the other two being 100 Å columns. The IR instrument was a Perkin Elmer Model 521 Infrared Spectrophotometer.

Method

Gel-Permeation Chromatography

Vials containing samples of various fluids aged under various conditions were obtained from Rocketdyne. A 50 µl sample was withdrawn from each vial and diluted with 10 ml of tetrahydrofuran (THF) drawn from a bleed line immediately before the solvent pump on the chromatograph. When the sample was thoroughly dissolved, the flasks were purged with nitrogen to prevent oxidation of the THF. To minimize the effects of degradation that might occur while in solution, the solutions were never allowed to stand more than 30 minutes before injection into the chromatograph. Injection volumes varied between 50 and 120 µl depending upon the intensity of the peaks and the equipment sensitivities. Most injections were 60 µl.

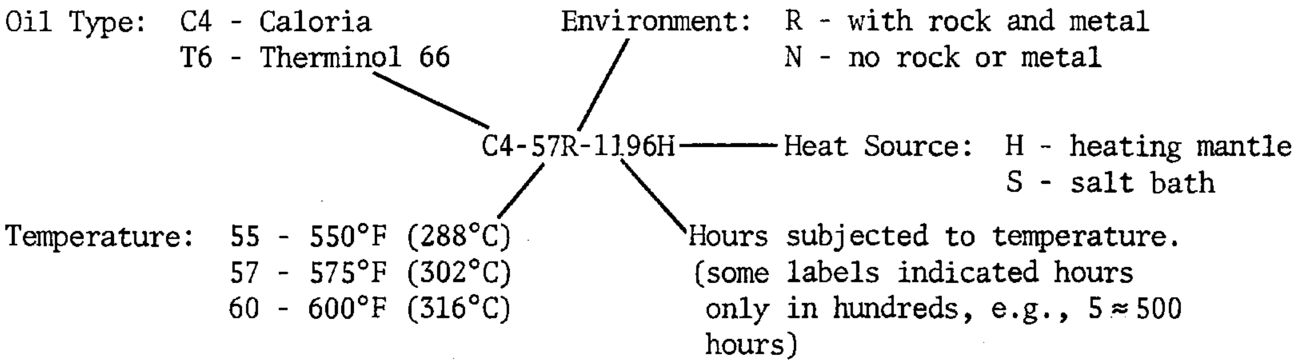
THF was used as the carrier phase for all the GPC runs, with special precautions taken to maintain a nitrogen blanket over the solvent to minimize oxidation and, consequently, instrument baseline drift. The solvent flow rate in all cases was 2.0 ml/min. The UV detector was set at a wavelength of 254 nm, and the sensitivities and attenuation of both detectors adjusted for optimum chart recording.

IR

All runs were made using a liquid cell with sodium chloride windows and a 0.1-mm path length. Scans covered wavelengths from 2.5 to 25 microns.

Nomenclature

Samples were labeled according to the following key:



Oil Type: C4 - Caloria
T6 - Therminol 66

Environment: R - with rock and metal
N - no rock or metal

C4-57R-1196H

Heat Source: H - heating mantle
S - salt bath

Temperature: 55 - 550°F (288°C)
57 - 575°F (302°C)
60 - 600°F (316°C)

Hours subjected to temperature.
(some labels indicated hours only in hundreds, e.g., 5 ≈ 500 hours)

For purposes of identification, the peaks in the UV absorbance profile were assigned numbers indicative of their retention times; viz. the 462 peak had a nominal retention time of 4.62 minutes or 4 minutes, 37 seconds. As there was only one sharp peak in the RI profile, no identifying symbol was chosen.

Observations

Table I lists all of the samples that were actually analyzed. Because the most interest was centered on Caloria HT 43, GPC runs were not done on any Therminol 55 samples and IR scans were not done on any of the Therminol 66 or Therminol 55 samples. (Note: Therminol 55 was of little interest because of very high weight loss, and Therminol 66 was of diminishing interest because of high unit cost and weight loss rates comparable to Caloria HT 43.)

A standard Caloria HT 43 GPC run is shown in Figure 1. The molecular weight profiles have the larger or heavier weight molecules on the left-hand portion and the lighter or smaller molecules on the right-hand side. The top profile is for UV absorbance and the bottom for RI.

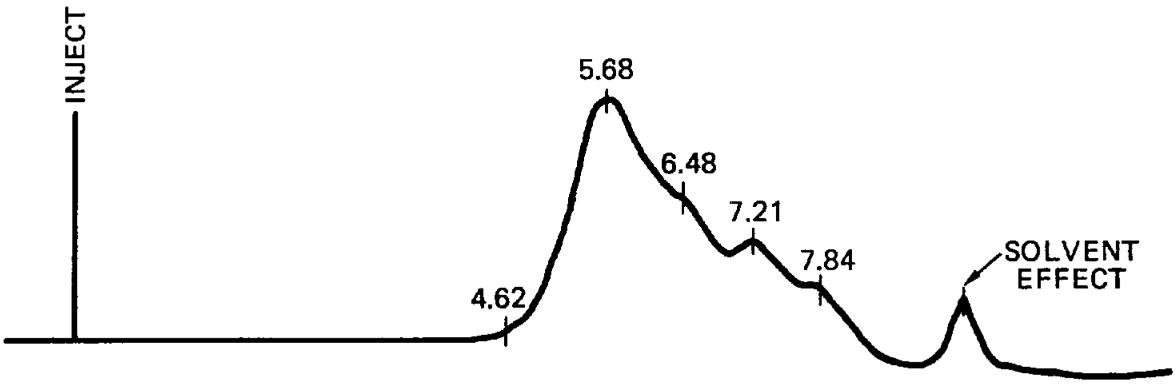
There are three peaks of interest in the Caloria HT 43 UV profile because of their location and activity. (Activity refers to the tendency of a particular peak to change its location or size with different exposure times.) In general, the intensity of the UV absorbance peaks was directly proportional to exposure time; however, in all cases the relationship was nonlinear, i.e., increasing the rate of change with time. Analysis of samples from a particular test at various exposure times made it easy to predict the UV absorbance for the next sample in the series. In fact, the change in the shape and height was extraordinarily predictable for the 462 peak and 568 peak, but somewhat less predictable for the 784 peak. Figure 2 shows a plot of peak height versus exposure time for three series at different temperatures; the similarity in changes is very obvious. The change in intensity of the 462 peak parallels that of the 568 peak in most circumstances, which appears to be somewhat of a paradox since it is so much smaller at first. The predictability in peak height is also somewhat anomalous because of the lack of similarity between the weight loss and viscosity change data as reported by Rocketdyne[8] (see Figures 3 and 4); however, the intensity of the 784 peak does have a strong correlation with this data.

The activity of the 784 peak is very complex, as it not only has a somewhat unpredictable intensity change, but also undergoes significant shifts in location. If the size of the 784 peak is compared to its equivalent position on the RI profile, it becomes apparent that the peak could contain either a high "concentration" of those chemical groups that cause UV absorbance or

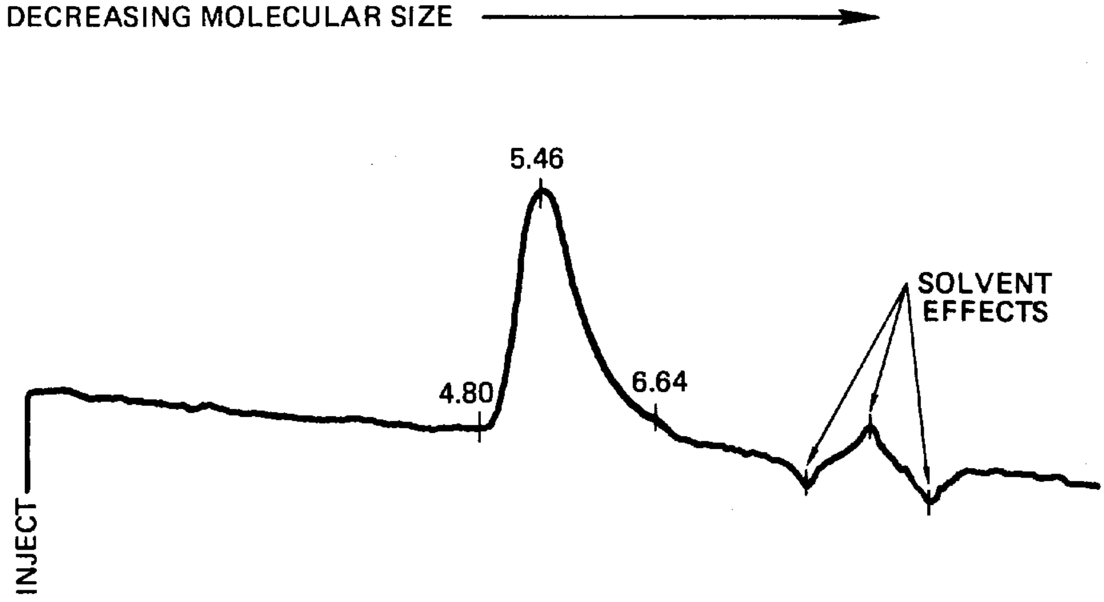
TABLE I

Sample	(HR)	GPC	IR
C4-60R-5H	(500)	x	x
" 12H	(1299)	x	x
" 20H	(2000)	x	x
C4-60R-10S	(1020)	x	x
" 20S	(2027)	x	x
C4-60N-5H	(500)	x	x
" 11H	(1189)	x	x
" 18H	(1890)	x	x
C4-60N-11S	(1171)	x	x
" 21S	(2178)	x	x
C4-60R-1008S		x	
C4-60N-1008S		x	
C4-57R-572H		x	x
" 1299H		x	
" 2000H		x	
" 3028H		x	
" 4035H		x	
" 5159H		x	x
C4-57R-1024S		x	
" 2024S		x	
" 3148S		x	x
C4-57N-1241S		x	
" 2248S		x	x
C4-55R-512H		x	x
" 1287H		x	
" 1987H		x	
" 2971H		x	
" 3978H		x	
" 5102H		x	x
C4-55R-976S		x	
" 1983S		x	
" 3107S		x	
C4-55N-1196S		x	
" 2203S		x	
" 3327S		x	

Sample	(HR)	GPC	IR
T6-60R-842H		x	
" 1303H		x	
" 2010H		x	
" 3017H		x	
T6-60N-1195S		x	
" 2202S		x	
" 3210S		x	
T6-57R-1024S		x	
" 2031S		x	
" 3155S		x	
T6-57N-1266S		x	
" 2273S		x	
" 3397S		x	
T6-55R-956S		x	
" 1963S		x	
" 3087S		x	



UV ABSORBANCE PROFILE



REFRACTIVE INDEX (RI) PROFILE

Figure 1. Caloria HT 43 Standard (dissolved in Tetrahydrofuran)

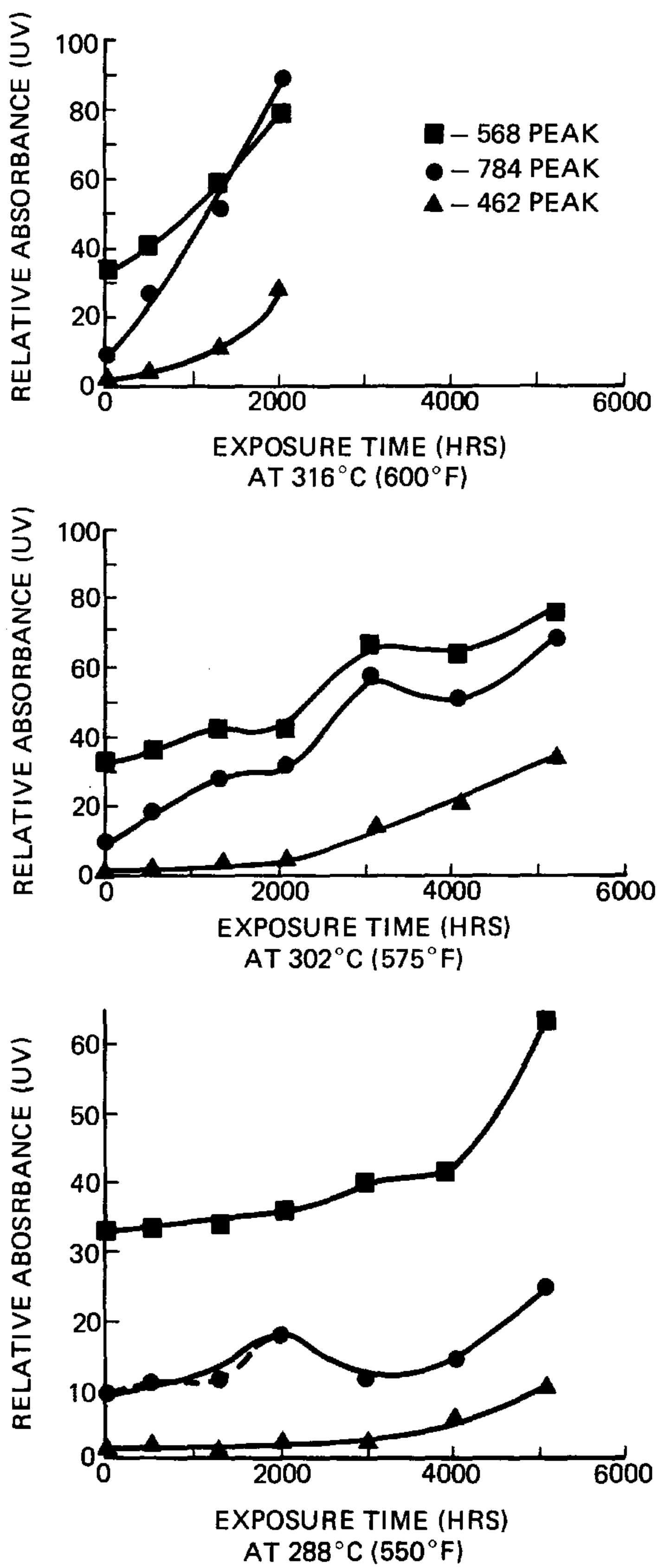


Figure 2. Relative Absorbance (UV) of Caloria HT 43 Peaks (Caloria with rock and metal heated with heating mantle) Versus Exposure Time

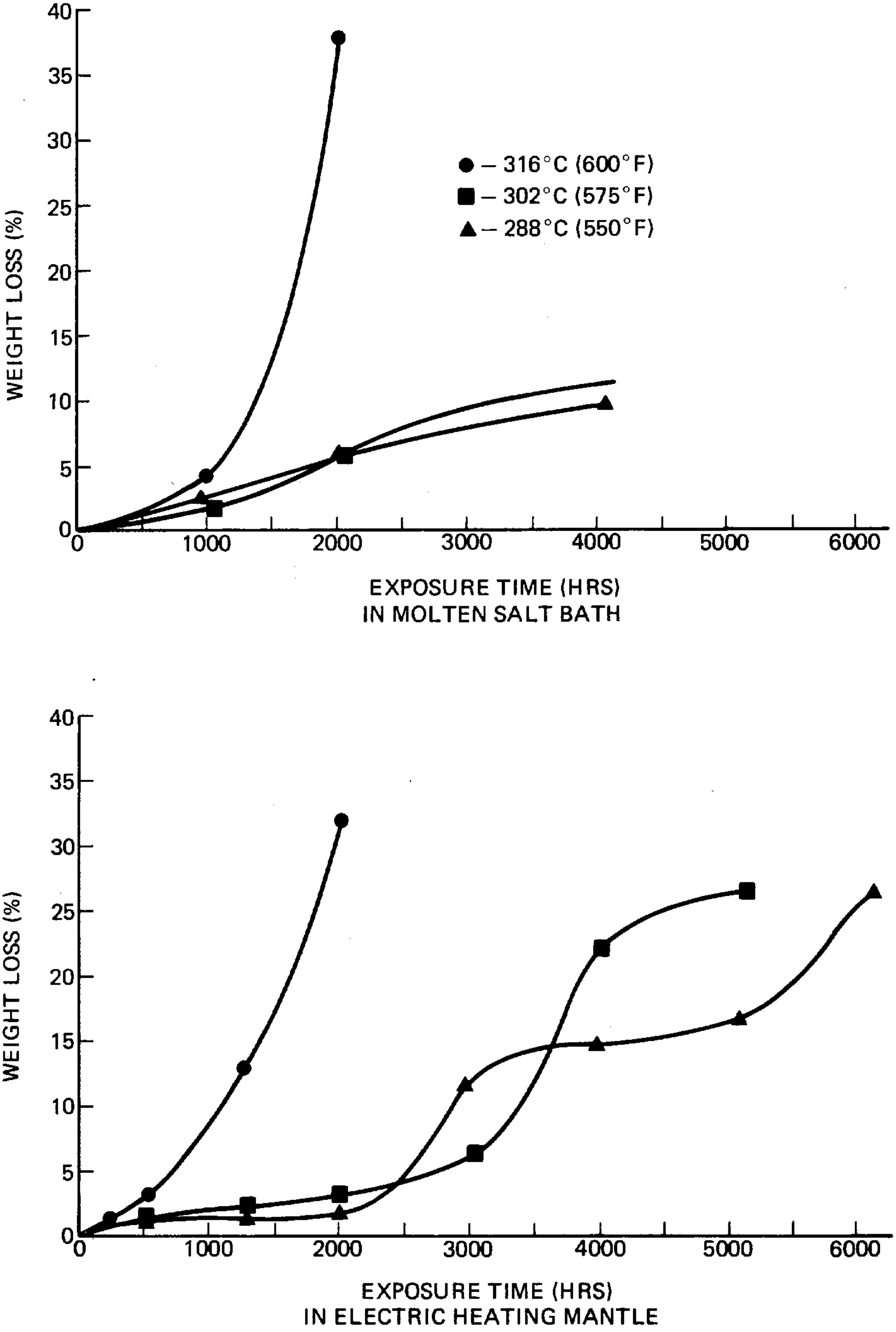


Figure 3. Weight Loss of Caloria HT 43 With Rock and Metal[8] Versus Exposure Time

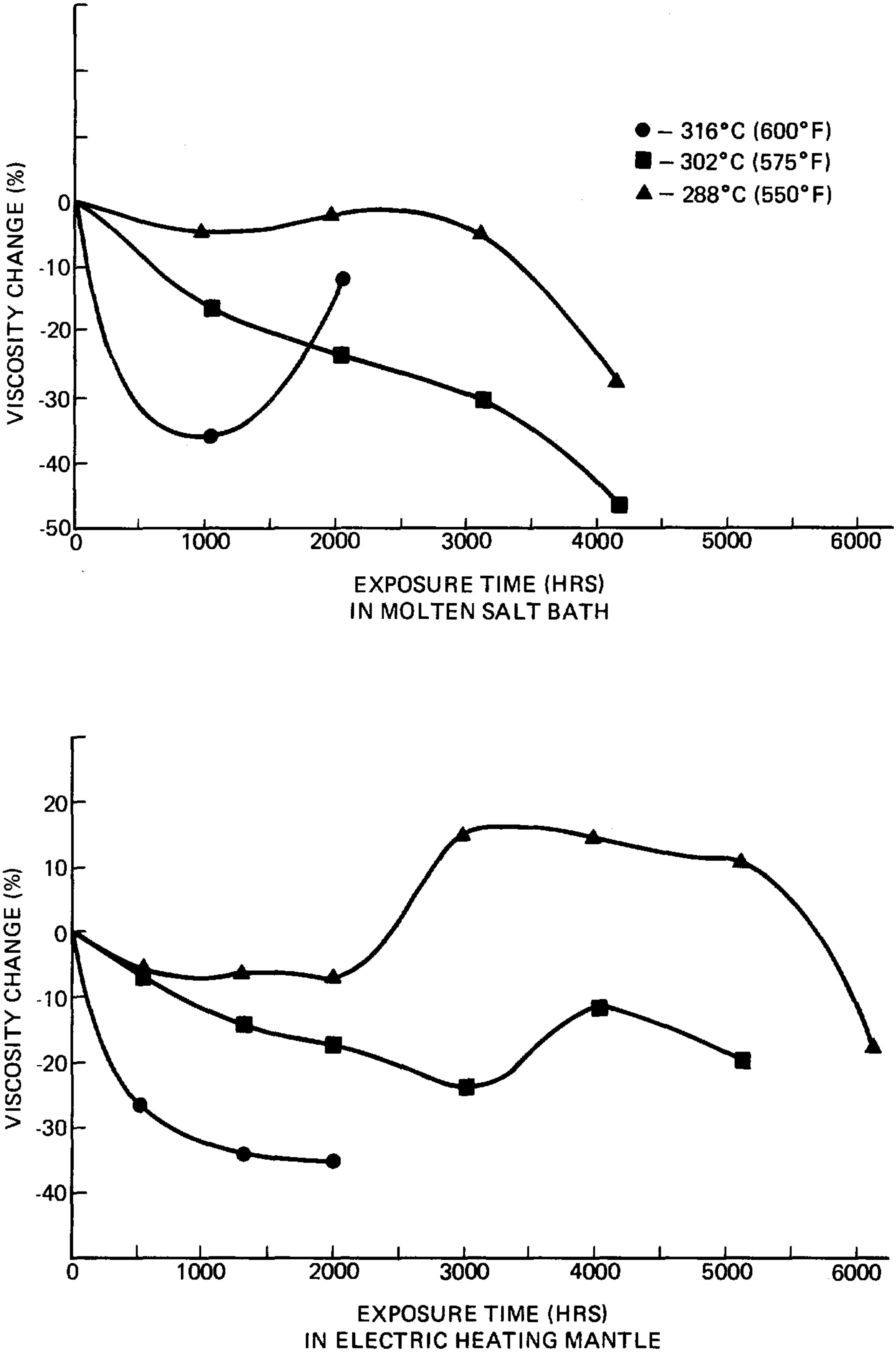


Figure 4. Viscosity Change of Caloria HT 43 With Rock and Metal[8] Versus Exposure Time

different chemical groups that have a higher UV absorbance. Also, because of the increased rate of change of this peak, one could presuppose that either (1) the chemical change that is occurring preferentially affects this portion of the molecular weight profile, or (2) this portion of the profile is essentially unaffected by the degradation mechanism and, by virtue of the fact that every other portion is being affected and ehnce being vented, its concentration in the remaining fluid is increasing. It would be presumptous at this time to eliminate any of the above possibilities.

The RI profile of Caloria HT 43 showed very little change in comparison to the UV profile. The detector is not very sensitive to chemical changes, but rather to density differences, which are indicative of molecular structure. There is no major shift of the peak in the RI profile, but there is some activity in the region equivalent to the 784 peak. This region is a broad, flat "peak" that shows a height less than 5 percent of the major peak; it does have a complex activity that is equivalent to the 784 peak.

The IR spectra of the samples proved to be fairly uniform; no chemical groups were present other than those involving carbon-carbon and carbon-hydrogen bonding, with the exception of one sample which contained some C=0 bonding. Oddly enough, a sample from the same series but at a longer exposure did not show this band. The only significant change in the IR spectra was the appearance of an absorbance band for unsaturated carbon bonds. Since this is a fairly weak absorbance, its presence could have been masked in the fresh oil samples.

The oil undergoing mechanical shear degradation tests showed no signs of decomposition after 1680 hours of exposure.

After all the chromatographic runs were made, backordered GPC standards were finally received so that a determination of the molecular weight range of the oil could be made. In running the standards, it was found that we were operating very close to the upper molecular weight limit of the columns. Supposedly, the columns are good for molecular weights less than 700 when, in fact, a weight below 450 is more realistic (see Figure 5 for standard calibration curve). Suspecting that this operational mode could have hidden some polymerization effects, a 500 Å microstyragel column was added and several selected runs (long-term exposures at 317 and 302°C) were repeated to determine if peak shapes or relative position to the standard would change. There was very little, if any, change in the peaks. What variations were present could be attributed to instrument drift or temperature drift.

When compared to the test oils, the standard aliphatic oils of a similar molecular weight and configuration showed very little absorbance in the UV, and, in some cases, showed less absorbance than the carrier solvent (THF). It was noted that partially unsaturated standards demonstrated slightly higher absorbance than the completely saturated standard of equivalent carbon number.

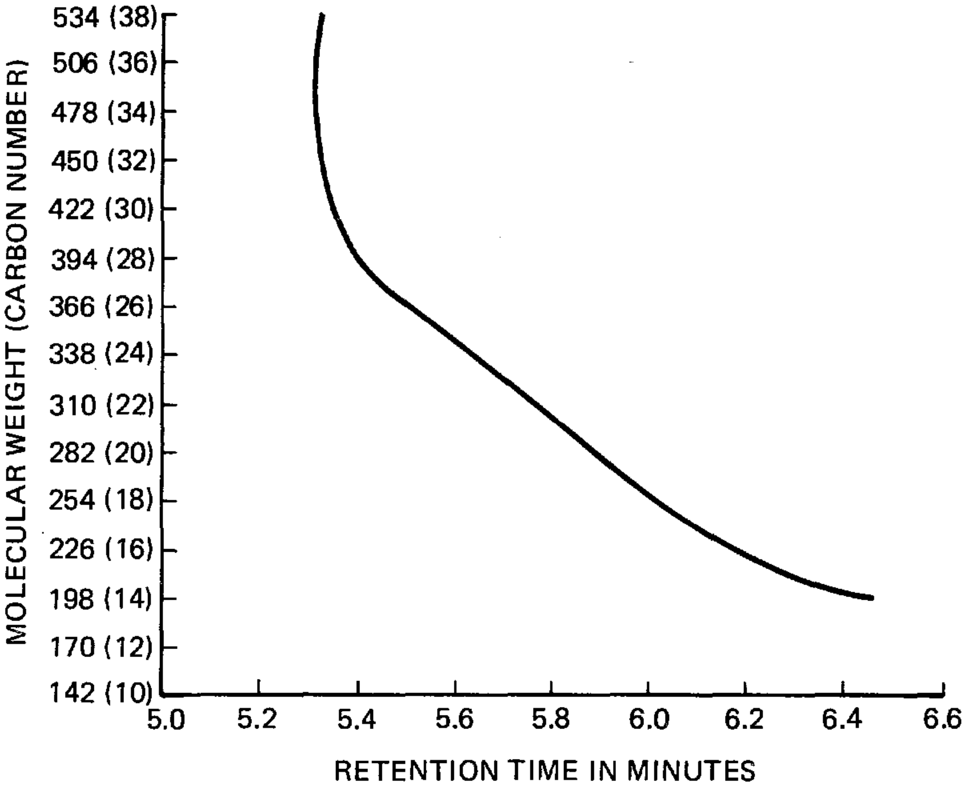


Figure 5. Molecular Weight (carbon number versus retention time)

Conclusions

1. Comparison of fresh Caloria HT 43 to standard aliphatic compounds indicates that the bulk of the oil has a mean molecular weight of approximately 380, corresponding to a 27 carbon chain. The approximate molecular weight range is from 170 (difficult to determine at such low values) to 550. The fresh oil is evidently not entirely aliphatic; the pure aliphatic standards of approximately the same molecular weight show essentially zero absorbance at 254 nm, whereas the fresh oil sample demonstrated a significant absorbance at this wavelength. The IR spectra of the fresh oil showed no definite evidence of unsaturation, but it may have been masked by other broad absorbance bands that are indistinct.

2. There is a great deal of thermal cracking occurring in the Caloria HT 43. Since there is no major shift in the main peaks of either the UV or RI profile, I believe that the cracking is not a one-step process. Rather than breaking off very small molecules from a large chain, the mechanism seems to be the breaking of large chains in half, with subsequent division to smaller molecules which could then be lost in venting (which was the case for the Rocketdyne tests). This mechanism would also account for an increase in the intensity of the 784 peak, which roughly corresponds to 1/2 of the mean molecular weight of the fresh oil.

3. In most of the Caloria HT 43 samples, there is no conclusive evidence of polymerization. However, the leading edge of the RI profiles for a few samples does show some indication of polymerization. The profile does not start upward as sharply as in the fresh oil, and yet, comparisons of the sample to the fresh oil reveal that the remainder of the profile is identical. From this, the degree of polymerization in the worst case was calculated to be less than 1 percent after 2000 hours at 316°C.

4. The change in UV absorbance for Caloria HT 43 over the entire molecular weight profile is probably due to a dehydrogenation reaction. Considering the testing that was conducted, this is the only chemical change that the author feels would affect the entire molecular weight range. If the change in UV absorbance were attributable to a particular compound of high UV absorbance, it would show up as a separate peak in the GPC. Also, since many of the oil samples were heated in inert environments, there was no source of additional elements to cause this change in UV absorbance through the formation of different chemical groups. Rearrangement of molecular configurations could cause some change in UV absorbance, but the changes would not be nearly as large as those observed.

5. It has been theorized[1] that the degradation products of oils similar to Caloria HT 43 act as catalysts for further degradation. The question of

auto-catalysis is very difficult to answer at this time, and I do not believe that any further analysis of the data will enable us to do so. There is much to suggest that considerable activity is present in the oil, but because of the variety of environments that the various oil samples experience and because of the apparently conflicting data, it is very hard to determine exactly what is the cause of this activity. To be more specific, examination of the weight loss curves[8] for Caloria HT 43 at 302°C (575°F) reveals significantly different behavior for the oil heated in a salt bath compared to oil heated with a heating mantle. In all other respects, the oils experience the same environment, yet the curves differ except for exposures of less than 1000 hours. Why should the method of heating affect the weight loss curve unless one method maintains a more constant (and possibly higher) temperature? Even then, that does not explain why the curves cross. Attempts to reconcile this data with the viscosity change data introduce more contradictions even if we assumed consistent catalysis mechanisms for rock and metal, and absolute viscosity changes from aliphatic to olefinic hydrocarbons. I believe that the only approach is to conduct experiments that are specifically designed to answer this question.

6. If a linear relationship is assumed between UV absorbance and unsaturation, then there is approximately 5-10 percent unsaturated carbon-carbon bonds in the fresh Caloria HT 43 and as much as 50 percent unsaturation in samples aged as long as 5000 hours. These figures are at best approximations since UV absorbance is a function of conjugation, molecular size, and molecular configuration, all of which can be constantly changing. These rough estimates were calculated by UV absorbance comparison of partially unsaturated hydrocarbons of approximately the same size and configuration as the Caloria HT 43.

7. Because of the nature of the tests conducted at Rocketdyne, it would be improper to speak here of a degradation rate if it were not defined very specifically. These tests allowed an unknown fraction of decomposition products to be vented to the atmosphere after passing through a condenser. Therefore, some degradation products may have been condensed back into the system where they could play a role in autocatalysis. Yet, there may be (and probably is) a small amount of polymerization, and thus the total reaction rate should be defined by three terms:

   (a) R_{LR} = reaction rate for producing low boiling degradation products that were carried up the condenser but returned

   (b) R_{LV} = reaction rate for producing low boiling degradation products that were lost entirely in venting

   (c) R_H = reaction rate for producing high boiling degradation products

   Then the total degradation rate would be R, where

$R = R_{LV} + R_{LR} + R_H$

and the degradation rate for producing low boiling compounds would be

R_L where

$R_L = R_{LV} + R_{LR}$

The degradation rate that can be inferred from the Rocketdyne weight loss data is only R_{LV}. Approximations for R_H can be derived from the GPC data. If the correct processor is chosen, the R_{LR} reaction rate can be close to zero, and the total degradation rate can be less than 0.25 percent per week for continued exposure of Caloria HT 43 at 302°C. This rate would be considerably better than the rates of 0.46 percent per week and 0.86 percent per week found in the Rocketdyne data[8] and the 0.93 percent per week reported by Dow.[2] This 0.25 percent per week value is determined by interpolating available data to very low exposure times and assuming the addition of a very small catalytic reformer for reconditioning the bulk fluid back to a more aliphatic oil.

8. If it is to be effective, a Caloria HT 43 processor should be capable of removing those compounds with a molecular weight less than 226 (equivalent to a 16 carbon molecule) and greater than 562 (equivalent to a 40 carbon molecule). This range would effectively "clean-up" the molecular weight profile to eliminate those fractions of high chemical activity.

9. Although there is no apparent degradation in Caloria HT 43 from the mechanical shear tests, it must be pointed out that the tests were run at room temperature (25°C) and that pumping at elevated temperature would certainly hasten any effect present. However, the volume of fluid in the pumps of a thermal storage system is extremely small in comparison to the total amount used, and therefore the fluid would have a much shorter exposure to this mechanical shear. All things being considered, it appears that any mechanical shear degradation effects would be completely overshadowed by the thermal degradation effects.

Summary

As a result of the investigation described herein, it is fairly safe to assume that the Caloria HT 43 under test experienced large scale thermal cracking, very little or no polymerization, a very significant amount of dehydrogenation (perhaps as much as 50 percent), and no continuous oxidation effects. Also, a properly designed processor should be capable of prolonging the usable lifetime of the oil. The exact nature of the processor, other than a straightforward fractional distillation column, can only be determined by additional testing.

The degradation that most oils will undergo during actual commercial applications should be predominantly due to thermal conditions and not due to mechanical shear.

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APPENDIX A--DESCRIPTION OF ROCKEYDYNE TESTS

Figure A-1 is a schematic representation of the test configuration used by Rocketdyne for their experiments. The flask was nominally 1000 ml, and the metal lathe turnings consisted of both stainless steel and carbon steel. The condenser above the flask is air cooled, and the entire apparatus was purged with nitrogen gas prior to heating. A slow nitorogen bleed was maintained during the course of the tests to prevent oxidation. Approximately 10-15 ml of oil were withdrawn every 1000 hours for evaluation.

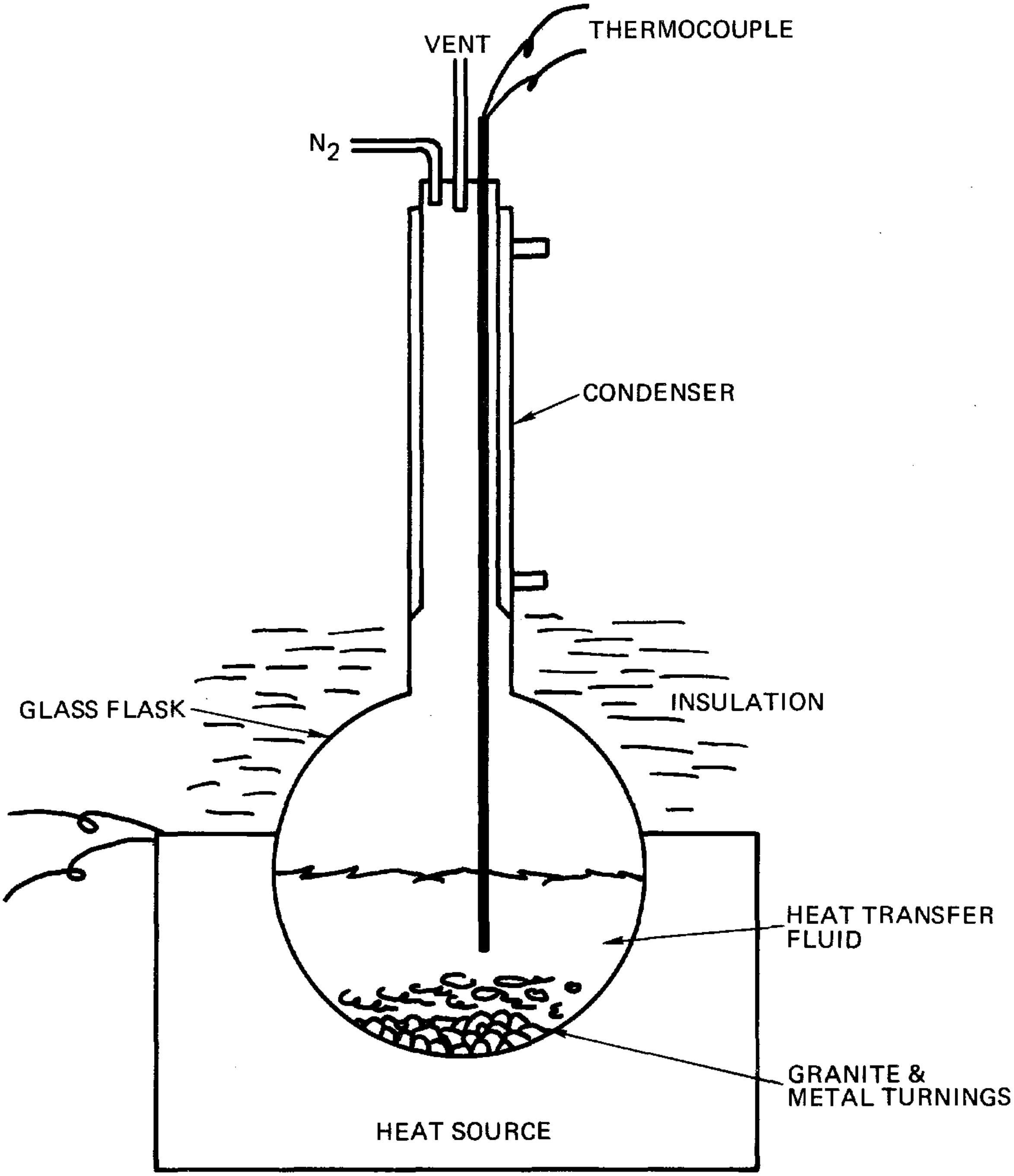
VENT
THERMOCOUPLE
N$_2$
CONDENSER
GLASS FLASK
INSULATION
HEAT TRANSFER FLUID
GRANITE & METAL TURNINGS
HEAT SOURCE

Figure A-1

APPENDIX B--DESCRIPTION OF MECHANICAL SHEAR DEGRADATION TESTS

Figure B-1 is a schematic representation of the test configuration at Sandia to give a preliminary indication of mechanical shear degradation. The motor of the stirrer was separated from the samples by a plastic bag to minimize the introduction of dust and ozone into the sample. The speed and depth of the propeller were adjusted to preclude air bubble entrainment. The containers were 180-ml beakers, and the stirrer was a 3-1/2 in. diameter propeller spinning at 2000 rpm.

MECHANICAL SHEAR DEGRADATION
EXPERIMENTAL TEST SETUP

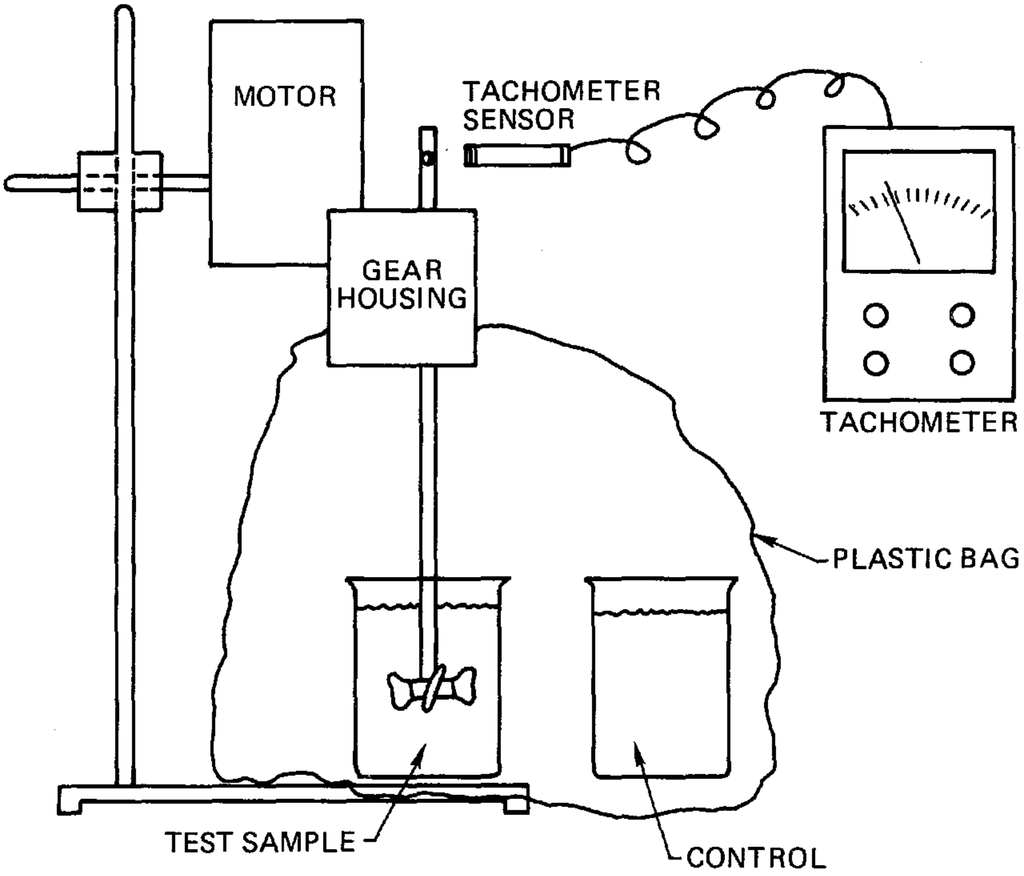

Figure B-1

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