NAVAL AIR PROPULSION TEST CENTER

TRENTON, NEW JERSEY 08628

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A STUDY OF THE FACTORS AFFECTING DEPOSITION CHARACTERISTICS OF SYNTHETIC LUBRICANTS FOR GAS TURBINE ENGINES

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The potential of the neopentyl polyol esters to survive higher surface temperatures without forming excessive harmful coke deposits was investigated. This study consisted of an engineering evaluation of the lubricant deposition-degradation characteristics which could have a significant bearing on the maintainability and reliability of future high thrust to weight ratio engines to be incorporated into the Navy inventory. Relationships were then established between these characteristics

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and chemical composition of the basestock materials, and to a lesser degree, the oxidation inhibiting packages. The intention of this investigation was to provide cause and effect relationships for the phenomena which were either the strengths or weaknesses of the current formulation philosophies. Such an understanding would open the way to meet the more demanding future requirements.

It is equally desireable that engine designers utilize the information presented as a guideline for avoiding those environments which are most conducive to the generation of lubricant degradation products that can jeopardize engine operation.

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A STUDY OF THE FACTORS AFFECTING DEPOSITION CHARACTERISTICS OF SYNTHETIC LUBRICANTS FOR GAS TURBINE ENGINES

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INTRODUCTION

The gas turbine lubricant, as it performs its function as bearing lubricant and coolant, is surrounded by an environment that is conducive to its oxidative and thermal decomposition. A breakdown of the lubricant can seriously jeopardize engine performance since decomposition products, such as coke and sludge, interfere with the proper functioning of bearings, seals, oil scavenge pumps and breather systems. Severe failure of the lubricant in any one of these areas can produce conditions which will lead to catastrophic engine failure.

For more than a decade, Navy gas turbine aircraft engines have been operating on lubricants that are generally classified as neopentyl polyol esters. As a class, these lubricants possess satisfactory thermal and oxidative stability as well as the physical properties that permit operation over a wide temperature range. Since their introduction as MIL-L-23699 lubricants into Navy aircraft systems in 1963, oil drain intervals have been extended, consumption reduced, sludging virtually eliminated and coke formation decreased below levels experienced with the previously used diester type lubricants.

However, the ability of these oils will be tax l as designers strive to derive more power out of lighter more compact powerplants. With the resultant increase in what may be termed "energy density" of the engine, it was anticipated that the temperature of surfaces to which the lubricant is exposed would increase to the point where the present ester lubricants would decompose to form objectionable amounts of carbonaeceous deposits. Therefore, the Naval Air Propulsion Test Center (NAPTC) undertook a research program, authorized by reference 1, to determine what potential was inherent in the neopentyl polyol esters to survive higher surface temperatures without forming excessive harmful coke deposits. This study consisted of an engineering evaluation of the lubricant deposition-degradation characteristics which could have a significant bearing on the maintainability and reliability of future high thrust to weight ratio engines to be incorporated into the Navy inventory. Relationships were then established between these characteristics and the chemical composition of the basestock materials, and to a lesser degree, to the oxidation inhibiting packages. The intention of this investigation was to provide cause and effect relationships for the phenomona which were either the strengths or weaknesses of the current formulation philosophies. It was believed that such an understanding could open the way to new approaches in the development of lubricants needed to meet the more demanding future requirements.

It is equally desirous that engine designers utilize the information presented as a guideline for avoiding those environments which are most conducive to the generation of lubricant degradation products that can jeopardize engine operation.

Publication of this report completes the requirements specified by reference 1.

CONCLUSIONS

1. Improvement in ester lubricant technology is needed in order to provide satisfactory deposit characteristics when such lubricants are exposed to the anticipated environments of future Navy engines. Toward this end, the following findings can be considered:

(a) Quantitatively, deposit formation is a strong function of the chain length of the acid component of the basestock. Deposits increase with increasing chain length.

(b) The basestock alcohol component has a small effect on deposit weight with deposits increasing in the order dipentaerythritol, pentaerythritol and trimentylol propane.

(c) An interaction effect between acids and alcohols exists whereby the differences in deposit weights from two alcohols increase with increasing acid chain length.

(d) Qualitatively, deposit formation patterns are strongly dependent on the acid component of the ester. As acid chain length increases, the deposit area and temperature range over which deposits form increase while average temperature of the deposit forming zone decreases.

(e) The performance of single acid esters is identifiable in the performance of mixed acid esters. Therefore, mixed acid ester performance can be predicted by the performance of the component individual single acids.

(f) Evaluations of neat basestocks agree with the trends established for fully inhibited lubricants.

(g) Additive systems employed to control bulk oil oxidation contribute significantly to deposit formation.

2. The differences in the deposit forming tendencies among the lubricants typical of current (MIL-L-23699) technology can be considerably troublesome to engine designers striving to provide lubricant environments that are compatible with all lubricants within this class.

RECOMMENDATIONS

1. Findings of this investigation should be used as a basis for developing a new class of ester lubricants which can better withstand the (anticipated) more severe environments of future Navy engines.

2. Attention should especially be given to developing basestocks which, as a class, are very consistent in deposition characteristics and to developing additive packages which perform the necessary function of

inhibiting bulk oil oxidation without adding to the formation of objectionable types of deposits.

3. Future lubricant specifications should define those environments in which the formation of objectionable types of deposits is unavoidable. These definitions should then be utilized as guidelines by the engine designer to avoid engine lubrication and breather system configurations that are conducive to gross deposit formation.

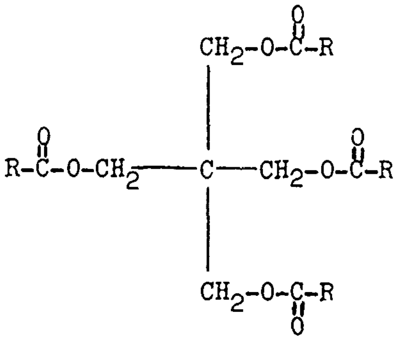
DESCRIPTION

Lubricants

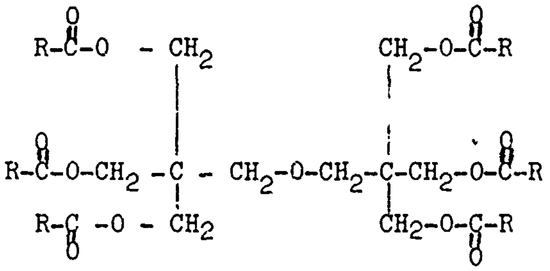
1. The gas turbine engine lubricants of concern to this research program are based on a group of "hindered" esters formed from organic acids and polyfunctional alcohols. These esters, known as neopentyl polyol esters, depend primarily upon a unique five-carbon structure in the polyfunctional alcohol used for esterification with the selected monofunctional acids. Polyols derive an added measure of thermal (pyrolytic) stability by virtue of the hinderence provided by the neopentyl structure which eliminates hydrogen from the "beta" carbon.

2. The esters most frequently employed in products that concern this program are mixed acid esters of pentaerythritol, dipentaerythritol and trimethylol propane. The chemical structures of these esters are shown below:

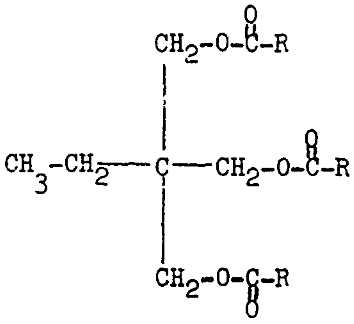
Pentaerythritol (PE)



Dipentaerythritol (DPE)



Trimethylol Propane (TMP)



For each of the above structures R=C_5 to C_{10} either straight or branched chain hydrocarbons, the chain length being derived from that of the monocarboxylic acid used for the esterification of the alcohol.

3. The neopentyl polyol esters are the basis for all lubricants qualified under specification MIL-L-23699 which currently meets the needs of all Navy gas turbine propulsion systems. In 1963, the Navy introduced these lubricants to replace the MIL-L-7808 lubricants which were classified as monohydric alcohol esters of dibasic acids. The hindered polyol esters have been shown to possess excellent thermal and oxidative stability up to 400°F. Additionally, they have most of the other properties of a good lubricant, including good viscosity-temperature characteristics, fairly low pour point, and good lubricity without the use of additives.

4. In order to meet the physical property requirements of the specification, the esters are generally produced from mixtures of acids of various chain lengths. The finished product then contains a statistical distribution of acid-alcohol combinations. It is the effects of the various monobasic acids on deposition characteristics that constitute the major effort under this program.

5. More detailed information on the chemical structure and specific properties and characteristics of neopentyl polyol esters is contained in references 2, 3 and 4.

Test Methods

6. The evaluations conducted under this program employed two test methods commonly used in the evaluation of deposition and degradation characteristics of gas turbine lubricating oils. The methods referred to are the High Temperature Deposition (HTD) test and the Vapor Phase Coker (VPC) test.

High Temperature Deposition Tester

7. The HTD test simulates, with simplified equipment, the basic parameters that influence deposition and oil degradation throughout typical gas turbine engine lubrication systems. Deposition is defined as the formation, on a surface, of a solid or semi-solid material (e.g. varnish, coke or sludge) which is the result of decomposition of the lubricant upon contact with the hot surface. Degradation refers to the change in chemical structure, usually evidenced by changes in viscosity and acid number, of the lubricant due to its thermal and/or oxidative decomposition in the bulk state.

8. The apparatus used for HTD testing is the Alcor Deposition Tester, Model HTDT1003, manufactured by Alcor, Inc. of San Antonio, Texas. Figure 1 presents a schematic drawing of the test section. Oil is circulated at 300 ml/min by a high temperature pump. Since this is a precision constant displacement pump, constant flow is maintained by a constant-speed drive. Air, saturated with distilled water, is injected into the oil just prior to entering the deposition tube section. After leaving this section, the oil-air mixture discharges into a sump where oil temperature is maintained at the desired value by a controlled flow of an air-water mist that passes through a jacket surrounding the oil chamber. A filter screen is incorporated in the bottom of the cooler-sump. The oil level may be observed from the sight glass, and the level is maintained by the automatic leveling device.

9. The deposition tube is seamless (Type 440) stainless steel and the test area is 1/4 inch in diameter and 10 inches long. The tube is heated by passing AC current directly through the metal. Two thermocouples are inserted into the inside of the tube. One thermocouple enters from the bottom and is positioned at exactly three inches from the centerline of the oil inlet point for monitoring the tube temperature (5-3/4 inches from the bottom). Another thermocouple is located at the maximum temperature point, which is 3/4 inch from the oil outlet centerline (3-1/2 inches from the top end of the tube). The increase in the upper tube temperature point is an indication of the deposit build-up. All metal components contacting the test oil are stainless steel except for the pump which is made of high temperature steel.

10. The entire test section is enclosed in an insulated cabinet in which temperature is controlled by forced convection of air through a 3000 watt heater. The test rig is equipped with a total of six thermocouple probes, the outputs of which are recorded on a six-point strip chart recorder as follows:

a. Maximum deposition tube temperature

b. "Lower" deposition tube temperature (control point on lower end of tube).

c. Oil-out temperature.

d. Oil-in temperature.

e. Cabinet ambient temperature.

f. Bus bar connector temperature (used for test integrity purposes).

Dual thermocouples are utilized for controlling and recording the oil-in temperature and the cabinet ambient temperature.

11. The test conditions applicable to this method are as follows:

Oil-in Temperature	300°F ±2°F
Initial Oil Charge	250 ml ±20 ml.
"Lower" Deposition Tube Temperature	500°F, 525°F, or 550°F
Air Injection	1000 ml/min ±15 ml/min
Cabinet Temperature	200°F±5°F
Bus Bar Connector Temperature	100°F to 130°F
Test Duration	48 hours ±0.5 hr.

The above test conditions result in a temperature gradient along the tube with initial maximum tube temperatures in the order of 590°, 640° and 700°F corresponding to the lower tube temperatures of 500°, 525° and 550°F. For a fluid which forms little or no deposits, the temperature rise of the maximum temperature point will only be slight whereas for a fluid which forms heavy deposits this temperature will gradually increase and is indicative of deposit build-up at that point.

12. The complete method of test is described in detail in specification XAS-2354A (reference 5). The only deviation from this method is the variation in "lower" deposition tube temperature.

<u>Vapor Phase Coker Tester</u>

13. The VPC test simulates, in a simplified rig, those portions of a gas turbine engine where hot surfaces are contacted by oil mists and/or vapors only, i.e. no oil washing occurs at these surfaces. The test is used primarily to assess the tendency of lubricants to form deposits either as mists contact the hot surfaces or as vapors condense in cooler regions and reflux over hotter surfaces.

14. The test apparatus used for VPC testing is the Eppi Vapor Phase Coker, model 5400, manufactured by Eppi Precision Products, Inc. of Claredon Hills, Illinois. The Eppi Coker (Figure 2) consists essentially of a three neck flask (oil reservoir) surrounded by an electric heating mantle, an intermediate "heating" tube surrounded by a coiled rod type heater, and a stainless steel "vent" tube inside which the deposits are formed. In operation, air is fed through a tube entering one neck of the flask, bubbled through the oil and permitted to escape through the center neck. Upon leaving the flask, the air and vapors pass through the heater tube and then directly into the coking "vent" tube, where the deposits are formed. A thermocouple is inserted through the third neck of the flask and immersed in the oil for monitoring and controlling oil temperature. A second thermocouple is located in the heater. Temperature profiles of the vent tube are determined by means of a specially instrumented reference tube. The capacity of the oil reservior flask is 2000 ml. The stainless steel coker tube is 6 inches long, 0.5-inch on the inside diameter with a 0.049-inch wall thickness.

15. The conditions applicable to the VPC test are as follows:

Bulk Oil Temp. (Sump)	400°F
Tube Heater Temperature	Variable
Air Flow	0.027 scfm (dry air)
Time	17 hours

16. More complete details of the test method and equipment are found in Appendix A of this report.

DISCUSSION

1. At the initiation of this program, several gas turbine engine lubricants of the neopentyl polyol class were in use by the commerical airlines and the U.S. Navy. These products represented several years of research effort on the part of ester manufacturers and lubricant formulators. Their advantages in bulk oil stability, cleanliness and consumption over the diester lubricants, having been demonstrated in the laboratory, were confirmed by flight evaluations through rapid and wide acceptance by the airlines and by early Navy operating experience.

2. Among the products qualified against MIL-L-23699 were several formulations resulting from various research and development efforts to produce fluids that would meet the performance criteria of the specification. The basestocks of these products consisted of mono, di, and tri- pentaerythritol esters (hereafter designated PE esters) or mixtures of trimethylol propane and pentaerythritol esters (hereafter designated TMP/PE esters). Within these basestock categories, oxidation inhibition was achieved by several different types of additive packages.

3. Each of these lubricants was designed to meet the needs of existing gas turbine engines. In laboratory evaluations, as well as in actual service, no large differences in performance characteristics were observed among these lubricants. However, since it was anticipated that future military engines would impose more severe thermal requirements on these oils, it was decided to evaluate representative formulations at temperatures exceeding those applicable for current engines.

Evaluation of Current Technology - Phase I Testing

HTD Test

4. The rationale behind this first testing phase was to explore what potential for higher temperature operation existed in fluids developed by the current technology and to reveal what new approaches for research were indicated. These investigations were concerned with the bulk oil stability and particularly the deposition characteristics as affected by the basestock composition of the lubricant. For this purpose, the High Temperature Deposition (HTD) Tester was chosen as the research tool for evaluating the performance of seven formulations (5 PE and 2 TMP/PE esters).

5. The lubricants tested are identified by code numbers which categorize the products by basestock and additive composition (e.g. PE-1 or TMP/PE-5). In the case of the fully blended oils, PE means a basestock consisting of mono, di or tri-pentaerythritol esters. TMP/PE means that trimethylol propane esters are the dominant basestock components with mono, di or tri pentaerythritol being minor components. The number in the coding identifies an additive package concept. Note that the codes PE-5 and TMP/PE-5 would indicate the same type additive package in different basestocks.

6. The tests were conducted at three "control" temperatures i.e. 500, 525, and 550°F (see Description Section for test details). The two lower temperature tests were considered representative of the range of conditions existing in current operating engines. The 550°F test simulated the estimated environment of future engines.

7. The results of the Phase I testing are plotted on Figures 3 to 7 and the data are presented in Appendix B. The bar graphs of Figures 3, 4, and 5 show the effects of basestock, additive package and temperature on the three selected evaluation parameters: deposit formation, viscosity change (Δ V) and Total Acid Number change (Δ TAN). The data for the 500°F and 525°F test conditions demonstrate generally how, regardless of basestock or additive package, the performance is not significantly different.

8. It is quite obvious from inspection of the plotted data that the most pronounced effects on all three evaluation parameters are caused by raising the temperature above the range indicative of current engine environment, i.e. to 550°F. In this environment, bulk oil degradation

(Figures 4 and 5) becomes significant in most cases, whereas the effect on deposits is not very significant for four of the five PE esters. This observation is especially noteworthy since the main thrust of this study was the evaluation of the effects of basestock on deposition characteristics. Additive effects on performance are apparent from the plotted data, but their significance was not tested since the emphasis was on basestock effects. In comparing the PE and TMP/PE base esters, the assumption was made that equal levels of additive technology existed for both type basestocks and that the differences noted between basestocks (if real) were attributable to the response of the basestock to oxidation inhibition by additives as well as to inherent basestock stability. Therefore, to make comparisons between the basestocks, all data generated for each basestock was averaged for each test temperature. These mean values also include all repeat data on each formulation (see Appendix B).

9. To further illustrate both the temperature effect and the basestock effect, the mean values of the basestock data for each evaluation parameter are plotted versus temperature on Figures 6 and 7. From these plots, it is clear that the basestocks do not exhibit differences in any performance category at the two lower test temperatures. However, at the 550°F test condition, deposition formation appears to be widely variant between PE and TMP/PE with viscosity and TAN change displaying much smaller differences. If these differences are real, i.e. not the result of chance or experimental error, it could be said that the PE esters are superior to the TMP/PE esters in both deposit forming characteristics and bulk oil stability.

10. In order to assess the significance of the differences in performance displayed at 550°F on Figures 6 and 7, the data were subjected to statistical analysis which provided a means of distinguishing between real differences and differences caused by either experimental error or change. The analysis is included as a part of Appendix B. From the analysis, it was shown that, in the 550°F HTD test, a) the PE and TMP/PE ester lubricants possessed different deposit forming tendencies and b) no distinction could be made in their relative bulk oil stability characteristics (Δ viscosity and Δ TAN). Therefore, at this time in the evaluation, it was concluded that with the existing lubricant formulation technology, the PE ester lubricants were superior to the TMP/PE ester lubricants in deposition characteristics. With regard to bulk oil stability, the test method employed was not capable of discerning between the performance of the two ester basestocks.

11. During the course of the early investigations under this program, considerable experience had been gained from the use of polyol based lubricants in Navy engines (references 6 and 7). Inspections of engines had shown that carbonaceous deposit formation occurred predominantly in the non-oil-washed areas, i.e. either on surfaces contacted by fine mists of the lubricant or by condensed vapors in vent lines. Since the deposition data generated in the HTD tester was on oil washed surfaces, it was decided that the above findings would be more meaningful if some additional testing was performed in an apparatus where oil washing was

not present. The test rig chosen for this phase of the testing was the Eppi Vapor Phase Coker.

Evaluation of Current Technology - Phase II Testing

Vapor Phase Coker Test

12. The Vapor Phase Coker (VPC) testing was conducted, per the procedure of Appendix A, at a series of vent control temperatures ranging from 550°F to 750°F. The lubricants tested were the same as those used in the Phase I evaluations. The criteria for evaluation were the weights of the vent tube deposits which are shown in Figure 8 plotted against vent control temperature. Test results for this phase of the investigation are included in Table C-I of Appendix C. It should be noted here that the control vent temperatures are indicative of a selected test condition and are not the temperature of the surface on which the deposits were formed. Actual surface temperatures at the deposit locations can be determined from the tube temperature profile given in Appendix A. The relationship between actual surface temperatures and deposit formation will be discussed in later sections of this report.

13. Before proceeding with the analysis of the Phase II results, some general observations associated with the interpretation of results generated during this phase should be made. It can be noted from Figure 8 that, as control temperature is increased, deposit formation reaches a peak and then falls off as temperature is further increased. The maximum deposits were formed at the 700°F test condition for all lubricants tested except TMP/PE-6. However, for this lubricant as well as for each of the others, the difference in deposit weight between the 650°F and 700°F control temperature was quite small. The key point is the fact that all of the formulations, regardless of basestock composition or additive package, formed maximum deposits at approximately the same test condition.

14. Another observation, which was made by employing a glass vent tube, was that deposits are formed primarily from vapors that condense and/or from very fine droplets that agglomerate on the upper tube surface and reflux down to the hotter section. This refluxing material then forms hard carbonaceous or varnish type deposits as previously observed in the metal vent tubes. From these observations it was believed that there are several competing factors, e.g. surface temperature, volatility and stability of the refluxing material, that affect the formation of deposits. Volatility and surface temperature are the prime factors governing the residence time that the refluxed materials remain on the hot surface. The oxidative stability determines quantity and the type of the deposits formed.

15. It was also noted that, for the vent control temperatures used, deposits were always formed in the vent tube at locations of approximately equivalent temperatures. As an example, note from photographs of split tubes (Figure 9) that, as the vent control temperature is increased, the location of the deposits moves up the tube to the region approximately corresponding in temperature to that of the previous test condition. Therefore, it appears that, although the products leaving the sump were

subjected to different temperatures (in the individual tests) on their way to the vent tube, the deposits were formed in the same temperature regime on the tube surface. It is also clear from Figure 9 that the refluxing zone (area above deposits) diminishes as vent control temperature is increased. With this condition occuring, one might expect that reducing the length of the refluxing area would reduce the quantity of material available for deposition. The expected result would then be that as vent control temperature was increased the deposit levels would decrease. However, this was not the case as seen from Figure 8. This phenomenon may be explained by theorizing that, since the sump temperature was the same for all tests, the propensity to form deposits was altered as the partially oxidized esters leaving the sump passed through the heater section. Up to the 700°F vent control temperature, the increase in coking propensity outweighed the effect of reduced reflux area resulting from the shift in the temperature profile of the vent tube. Above 700°F, although coking propensity of the materials leaving the heater section may still be increasing, the combination of increased volatility of these materials and the decreasing reflux area result in a lessening of the amount of the deposits formed. It is believed that this phenomenon represents a realistic approximation of what would occur in nes since the products which did not condense at the tube exit ature of 250°F would most likely be vented overboard from an actual ne and therefore would not be available for forming deposits.

16. Considering all of the above observations, it was concluded that evaluation of polyol type lubricants at either the 650 or 700°F test condition provided a realistic means of assessing performance at conditions most conducive to deposit formation. Having established a rationale for the interpretation of vapor phase coker results, the evaluation of the relative performance of the seven lubricants tested can be discussed.

17. An examination of the plots of deposit weights versus vent control temperature (Figure 8) supports the findings of the Phase I (HTD) testing that TMP/PE ester lubricants are more prone to deposit formation than those of the PE ester basestocks. This condition is especially apparent as the control temperature is increased as also was the case with HTD testing. At the 650°F and 700°F test conditions, those most conducive to deposit formation, lubricants TMP/PE 5 and 6 generated more deposits than any of the PE esters tested. Since this part of the evaluation was performed to confirm the trends seen in the Phase I testing and since general agreement was acheived, no statistical analyses into the significance of the observed differences were performed.

18. Photographs of the deposit formations in the vent tubes from the VPC testing at 650°F are shown in Figure 10. After weighing to determine the deposit weights, the tubes were split axially for examination of the deposits. The photographs show a very striking uniformity of appearance among the tubes within each basestock category. The PE esters developed a rather heavy (thick) deposit over a very short length of tube whereas the TMP/PE esters generated a thinner layer of deposits over a much longer

section of the tube. Considering the temperature profile of the tube (see Figure 10), the TMP/PE esters produced degradation products that were sensitive to deposit formation at lower surface temperatures and over a much broader temperature range than were the PE esters. This observation prompted further consideration into explaining the differences detected between the PE and TMP/PE lubricants.

19. The lubricants tested up to this point of the evaluation were all fully blended products containing additive packages tailored to meet specific requirements of Specification MIL-L-23699. The effect of additives on deposits within a basestock category was shown in the HTD testing of Phase I, and possibly these additives contribute to the differences in performance in the Phase II VPC testing, particularly within the PE ester category. Especially noteworthy is the fact that in both testing phases the PE-1 lubricant formed considerably more deposits than any of the other PE products. Whether or not the additives had an over-riding effect on either the quantity or the temperature sensitive range of deposits between the basestock categories was a subject of test Phase III.

20. Another factor to be considered regarding its effect on deposition was the average carbon atom chain length of the acid component of the ester. Since, in order to achieve the desired physical properties of this class of lubricant it is necessary to esterify TMP with longer chain acids than is necessary with PE, it was decided to assess the possibility that acid chain length was a dominant factor affecting deposit formation. For this purpose, the average deposit weights for the 650°F and 700°F test conditions (from Figure 8) were plotted against the average acid chain length of each lubricant (Figure 11). As was anticipated from the previous analysis, a trend of higher deposit level associated with the longer acid chain lengths of the TMP esters is quite apparent when considering all the data points of Figure 11. This data establishes that chain length can be very influential, but it is inconclusive because the two data points most responsible for the correlation with chain length are also the only data associated with TMP/PE esters. In order to exclude the alcohol basestock component, the PE ester results alone were considered. From inspection of the plotted data (Figure 11), a slight trend was conceivable, but unclear. Regression analysis confirmed (correlation coefficient =0.54) that these data could not support a chain length effect. However, repeatability of the test and the small differences among the PE ester besestock average acid chain lengths may have been responsible for the inability to discern the potential effect of chain length. Additional testing with neat base esters of specific and varying chain lengths would be required for the determination of the relative effects of alcohols, acids and additives.

Summary of Assessment of Current Technology

21. The evaluation of several qualified MIL-L-23699B oils in the first two testing phases of this program has produced the following conclusions concerning the current technology for this type of lubricant:

a. When subjected to test conditions considered representative of current engine environments, lubricant deposition and degradation characteristics were independent of either basestocks or additives employed in the various formulations.

b. In higher temperature environments, the PE ester lubricants' deposition characteristics were superior to those of the TMP/PE type, but it could not be determined (from the data available at the time) whether the differences were attributable to either the alcohol or acid components of the basestocks. Aside from the deposit formations being quantitatively different between the two basestocks involved, there were very consistent and distinct features associated with the particular basestock compositions. The PE ester lubricants formed deposits over a fairly small temperature range and at an average temperature which exceeded that for the TMP/PE based products. The TMP/PE esters formed deposits over a relatively broad temperature range.

22. It can, therefore, be seen that at "advanced" conditions the products developed by current technology exhibited varying performance characteristics. It was the cause of these characteristics that became the subject of the remainder of this program. It was believed that the establishment of the relationships between engineering evaluations of performance characteristics and lubricant chemistry would benefit and guide formulators in the development of the lubricants required for future gas turbine engines.

Evaluation of the Effects of Alcohol and Acid Composition on Deposition Characteristics of Esters - Phase III Testing

Vapor Phase Coker Test

23. The assessment of the effects of alcohol and acid components on deposition included Vapor Phase Coker testing of: a) basestocks of mixed acid esters in which the trimethylol propane (TMP) - pentaerythritol (PE) (mono or di) alcohol ratio was varied and b) single acid esters of DPE, PE (mono) and TMP esters. The mixed acid esters represent the type of basestock used in MIL-L-23699 oils and the results were used to show the response of deposit formation to both TMP-PE ratio and average acid chain length without the presence of additive effects. The single acid esters were used to separate the deposition response with respect to alcohol content and acid chain length.

24. This testing phase made use of the Vapor Phase Coker at the 650°F test condition. Experimentation with test conditions had shown that for evaluating uninhibited basestocks, the 650°F test gave good separation among the various esters with the deposits forming at tube locations where losses of vented products from the top of the tube would not

significantly affect results. In addition, a second evaluation parameter, "yield", was introduced. Yield is the weight of deposits formed expressed as a percentage of "through-put" (by weight) or the amount of lubricant that was lost from the sump and, therefore, passed through the vent tube. The yield is used in lieu of deposit weights in order to normalize the data with respect to the quantity of material available for the formation of deposits. This parameter is particularly useful in the evaluation of uninhibited basestocks of single acid esters where "through-puts" can vary over a wide range as the acid chain length is varied.

25. The effect of basestock components on deposition was studied by preparing test samples of various ratios of mixed acid esters of DPE and TMP and subjecting them to Vapor Phase Coker tests at 650°F. Test data are included in Appendix C (Table C-II). Deposit weights and yield versus DPE-TMP content are shown in Figures 12 and 13 respectively. These plots indicate the same trends observed from the results obtained with the inhibited lubricants. The higher the TMP content, the greater was the deposit formation.

26. However, it was also observed that these deposit levels were considerably lower than those generated by the inhibited lubricants. Note from Figure 8 that both TMP/PE inhibited esters formed deposits in excess of 450 mg at the 650°F test condition, but the maximum deposit for the neat basestock (also at the 650°F test condition) was about 300 mg (Figure 12). The yields likewise showed the same trend. The average yield for the two TMP/PE inhibited esters of Figure 8 is 5.72 percent whereas the maximum yield for the neat TMP/DPE esters is 1.04 percent (Figure 13). Of significance is the fact that, although the inhibitors grossly affected "through-put" (see Appendix C) and deposits, the results obtained on the neat basestocks still conform to the general trends established with the fully blended materials.

27. The assessment of the relative effects of TMP and PE esters continued by conducting VPC tests on a series of blends prepared from (mono) pentaerythritol tetravaleric ester (a single acid ester) and a trimethylol propane (mixed acid ester). Data from this testing is given in Table C-III of Appendix C. The yields obtained from these blends are plotted against PE-TMP content in Figure 13. Again the trend of increasing deposit level with increasing TMP content is quite apparent. It was also seen that the mixtures containing DPE (Figure 13) were somewhat lower in deposit forming tendency than those containing PE (mono-pentaerythritol).

28. Since the TMP used in the above blends has an average acid chain length of 7.9 as opposed to 5.0 and 6.2 for the PE and DPE respectively, one could also predict that the yield would increase with increasing chain length of the blend. This relationship is shown graphically in Figure 14. Least square regressions line through the data points show the definite relationship between yield and chain length. As anticipated, the correlation coefficients of 0.94 and 0.99 for the TMP/PE and TMP/DPE

blends respectively indicate a high degree of significance associated with this data, as was the case with correlation with TMP content (see Figure 13).

29. Photographic records of the deposit formation patterns in the vent tube for both sets of blends are given in Figures 15 and 16. By comparing the deposit distribution of the blends of TMP (mixed acids) and PE (C_5 acid only), Figure 16, to those of the fully inhibited oils, Figure 10, certain relationships between acid composition and deposit patterns are discernable. Valeric acid (C_5) is the dominant acid of the PE inhibited oils of Figure 10 and the deposits are distributed in a manner comparable to those on the left side of Figure 16 where the PE tetravaleric ester and, therefore, C_5 is dominant. As TMP ($C_{avg.} = 7.9$) begins to dominate the basestock blends (the right end photographs of Figure 16), the deposit patterns become more like the heavy deposit areas of the TMP/PE oils (Figure 10) where the C_7 and C_9 are the major acids. The thin deposit layer at the bottom of the TMP/PE -5 and -6 tubes is a characteristic of the additive package and, therefore, should be ignored when comparing to basestock (uninhibited) results. If the same type of comparison is made between the TMP/DPE blends (Figure 15) and the inhibited oils (Figure 10), the same trends with acid content are not apparent. However, in the case of the blends containing the DPE, the C_5 content was not as high as in those using PE. It should also be noted that the pattern of the deposit formation to the left in Figure 15 (high DPE content) is, as will be seen later, dominated by the DPE deposit characteristic.

30. In order to more clearly separate the effects of alcohols and acids, single (normal) acid esters of DPE, PE and TMP with acid chain lengths of 5, 7 and 9 were obtained. Since iso valeric acid (iC_5) is commonly used in the fully blended oils to achieve certain low temperature properties, it also was obtained for inclusion in this portion of the testing. Each of the above esters was then subjected to Vapor Phase Coker tests at the same conditions used for evaluation of the basestock blends. The resuls of the testing of these esters are reported in Appendix C (Table C-IV), and yield is plotted against the acid chain length in Figure 17. Note from the tables of Appendix C that the esters of iC_5 performed very much like those of the normal C_5 (nC_5) and therefore only the nC_5 results are used in the following analysis. The graphical presentation of the results (Figure 17) shows that deposit formation (yield) is very markedly affected by both the alcohol and the acid chain length. An interaction effect between the alcohol and chain length is also evidenced by the large differences at the C_9 chain length between TMP ester and PE esters compared to small differences at C_5. Therefore, at any particular acid chain length, TMP esters form the largest quantity of deposits with respect to throughput followed by PE and DPE esters. As the chain length is increased to C_7 and C_9, which is

typical of current practice to obtain the desired physical properties of TMP base lubricants, the propensity of the TMP ester to form hard deposits increases at a greater rate than that of the PE esters.

31. This analysis is based on "yield" which is a measure of the deposit forming tendencies per unit ester material available for conversion to deposits. Therefore, it represents a means of rating the relative quantities of deposits formed from a given quantity of the particular ester made available for conversion to solid products of degradation. It may be argued that the yield based analysis is not representative of what would occur in actual engine operation where, depending on bulk oil stability,various quantities of the particular acid esters would be available for deposit formation. It should be noted, however, from the data in Appendix C,that deposit weight, per se, would display the same trends as the yields, although the differences would not be as great.

32. These findings should not be mistaken as a measure of molecular stability of the esters. An analysis of relative inherent stability of the individual esters would entail a comparison of deposits formed with respect to the molecular weights of the esters involved. This would be necessary since, due to the various molecular structures of the esters concerned, molecules of equal stability could generate different quantities of deposition products. Detailed investigation into the relative resistance to decomposition of particular chemical species is beyond the scope of this program. It is not the stability of a particular molecule to resist pyrolysis or oxidation that is of concern here, but quantity and type of deposits that are formed from various chemical components as they undergo changes in a particular environment.

33. Therefore, as a result of the analysis performed thus far, it can be deduced that the pentaerythritol esters provide a more favorable basis than trimethylol propane esters for the development of lubricants for the more hostile environments of future engines. The analyses show a twofold reason for this conclusion - a) the PE and DPE alcohols produce esters which form less deposits than esters of TMP alcohols at equal acid chain lengths and b) PE esters, due to physical property requirements, employ shorter chain length acids which display lower deposit forming tendencies than the longer chain acids which must be used with the TMP esters. Of course this advantage could be less pronounced if physical property requirements were revised.

34. The deposit formation patterns of the single acid esters used for the above testing are shown in Figure 18. It is quite clear from inspection of the deposits in these tubes and the data of Table C-IV of Appendix C that the pattern of deposit formation is very strongly dependent on the acid component of the ester. Regardless of the alcohol component, the C_5 acid ester formed deposits over a short section at the lower (higher temperature) end of the tube. As the chain length increased to C_7 and then to C_9, the length of the

deposit areas increased and it occurred further up the tube (at a lower temperature) than the C_5 deposit area. These observations are displayed graphically on Figures 19 and 20. By careful visual examination of the deposit formations and by comparison to the tube temperature profile, the temperature at which deposit build-up was maximum and the temperature range of deposit formation were determined. The temperature at maximum deposit location is plotted against acid chain length for TMP and PE in Figure 19. DPE is not included in this plot since deposits were so light that a maximum build-up point could not be discerned. The graph shows how, as acid chain length increased from C_5 to C_9, the temperature at which maximum deposits formed decreased. It also shows that the TMP esters' maximum deposits occurred on surfaces with temperatures approximately 15° to 25°F higher than PE esters. Considering the subjectiveness involved in selecting the area of maximum deposits and possible small shifts in temperature profiles from test to test, the significance of such small temperature differences may be questioned. However, a comparison of the range over which deposits were formed between PE and TMP for the C_7 and C_9 acids supports the idea that the TMP esters form deposits at higher temperatures than PE esters.

35. In Figure 20, the least square regression lines for maximum and minimum temperatures at which deposit formation occurred are plotted against acid chain length for the combined data of the DPE, PE and TMP esters. This graph displays the fairly large temperature gradient (135°F) over which C_9 acid esters form deposits and the small gradient (70°F) over which C_5 acid esters are prone to deposition. Extending these ranges, via the tube temperature profile, to the tube length over which deposits form (Figure 20) it can be seen that the C_9 acid ester deposits are spread over an area 5 times greater than those of C_5 acid esters. This fact can be interpreted as an advantage for the esters produced with longer acid chains despite the fact that they form greater quantities of deposits. Inspection of the deposit formations (see Figure 18), especially for the PE and TMP esters, indicates how, at a given time, the smaller quantities of deposits formed with C_5 esters could result in a more severe physical or mechanical condition than would result from use of longer acid chain lengths. With both nC_5 and iC_5 esters of PE and TMP, the thick deposit formations are choking off a considerable cross-sectional area of the tube, but the C_7 and C_9 acid esters of the same alcohols have not yet "grown" out significantly from the surface. Therefore, the shorter acids may be more prone to causing such engine problems as vent line plugging or the formation of crusty deposits (sometimes called stringers) which easily break loose from the metal surface and migrate through the lubrication system.

36. A point in the above analysis that should be emphasized is that both the quantitative and qualitative trends indicated by the testing of single acid esters are also seen with mixed acid ester basestocks and with fully blended (inhibited) oils. As an example, Figure 21 compares the deposit formation patterns of: a) a single C_7 acid ester, a mixed ($C_{avg} = 7.5$) acid ester and a fully blended oil with a mixed

(C_{avg} = 7.5) acid ester basestock and b) a single C_5 acid ester and a fully blended oil with a mixed (C_{avg} = 6.1) acid ester basestock. In the above examples, C_7 and C_5 were major components of the respective mixed ester basestocks. Note also that for both examples the presence of oxidation inhibitors caused a slight upward shift in the deposit location. By examining the photographs of the tube deposits in Figure 21, the similiarities in deposit forming characteristics that exist between the single acid esters and the mixed acid esters containing acids of the same chain length as the single acid ester can be seen. The importance of this fact is that, by evaluating a single acid ester, inferences can be made regarding the effect (on deposition) of a single acid which is a major component of a mixed acid ester formulation.

Summary of Phase III Findings

37. The results of this phase of the evaluation are summarized as follows:

a. The quantity of deposits formed is a strong function of the chain length of the acid component of the basestock. Deposits increase as chain length increases from C_5 to C_9. The alcohol component has a lesser effect on deposit weights with increases occurring in the order DPE, PE and TMP. There is an interaction effect between acids and alcohols such that differences in deposits formed between PE and TMP esters are greater with C_9 acids than with C_5 acids.

b. The deposit forming patterns are also strongly dependent on the acid component of the ester. Although quantitatively forming less deposits, C_5 esters form thicker build-ups of deposits over a small area and temperature range. This area (covering a 0.8-inch length of tube, see Figure 20) occurs at temperatures ranging from 400°F to 470°F. As acid chain length increases, the deposit area and temperature range increase while the average temperature in the deposit area decreases. For example, C_9 acid esters form deposits at temperatures ranging from 250°F to 385°F which spans a 4-inch section of the tube. Although lesser in quantity, the deposits formed from the C_5 acids are more concentrated and, therefore, may result in build-ups that can lead to problems in shorter times than those formed from the longer chain acids.

c. The evaluation of single acid esters may be used to predict the deposition characteristics of particular acids when used as major portions of a mixed acid ester.

d. The results obtained on neat basestocks agree relatively with the trends established with fully inhibited lubricants.

FIGURE 1: HIGH TEMPERATURE DEPOSITION TESTER TEST SECTION SCHEMATIC

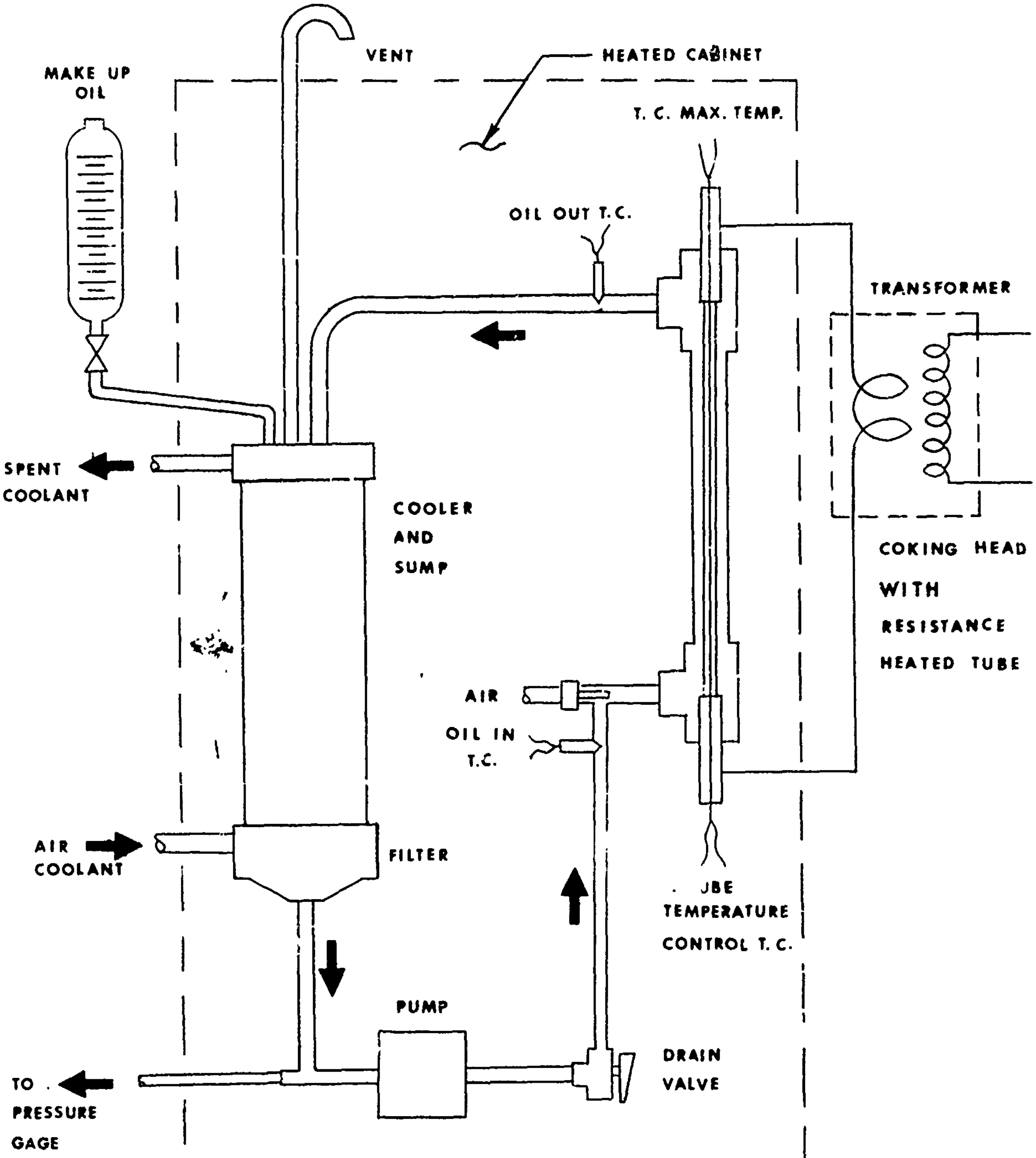


FIGURE 2: VAPOR PHASE COKER TEST SECTION SCHEMATIC

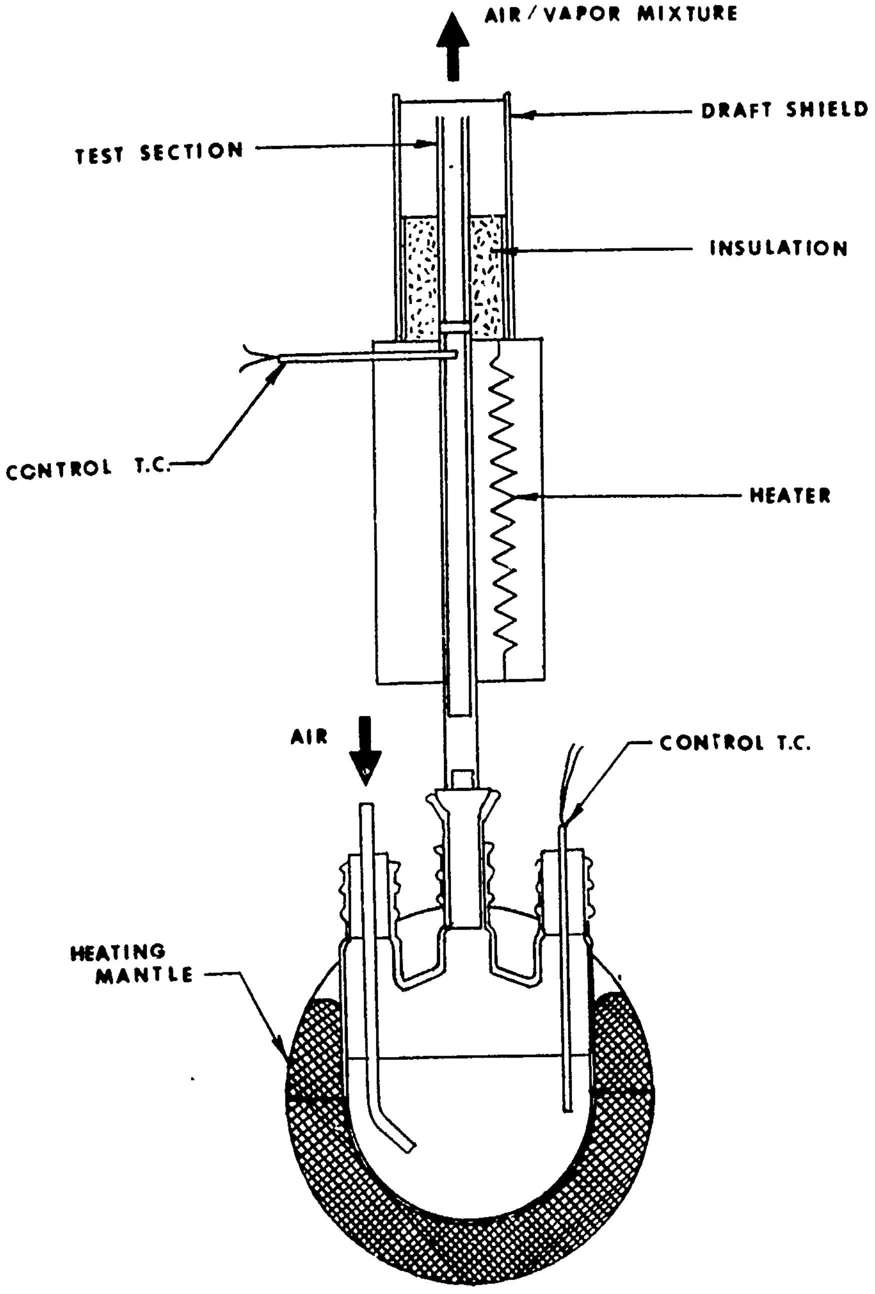


FIGURE 3: BASESTOCK AND ADDITIVE EFFECTS ON DEPOSITION

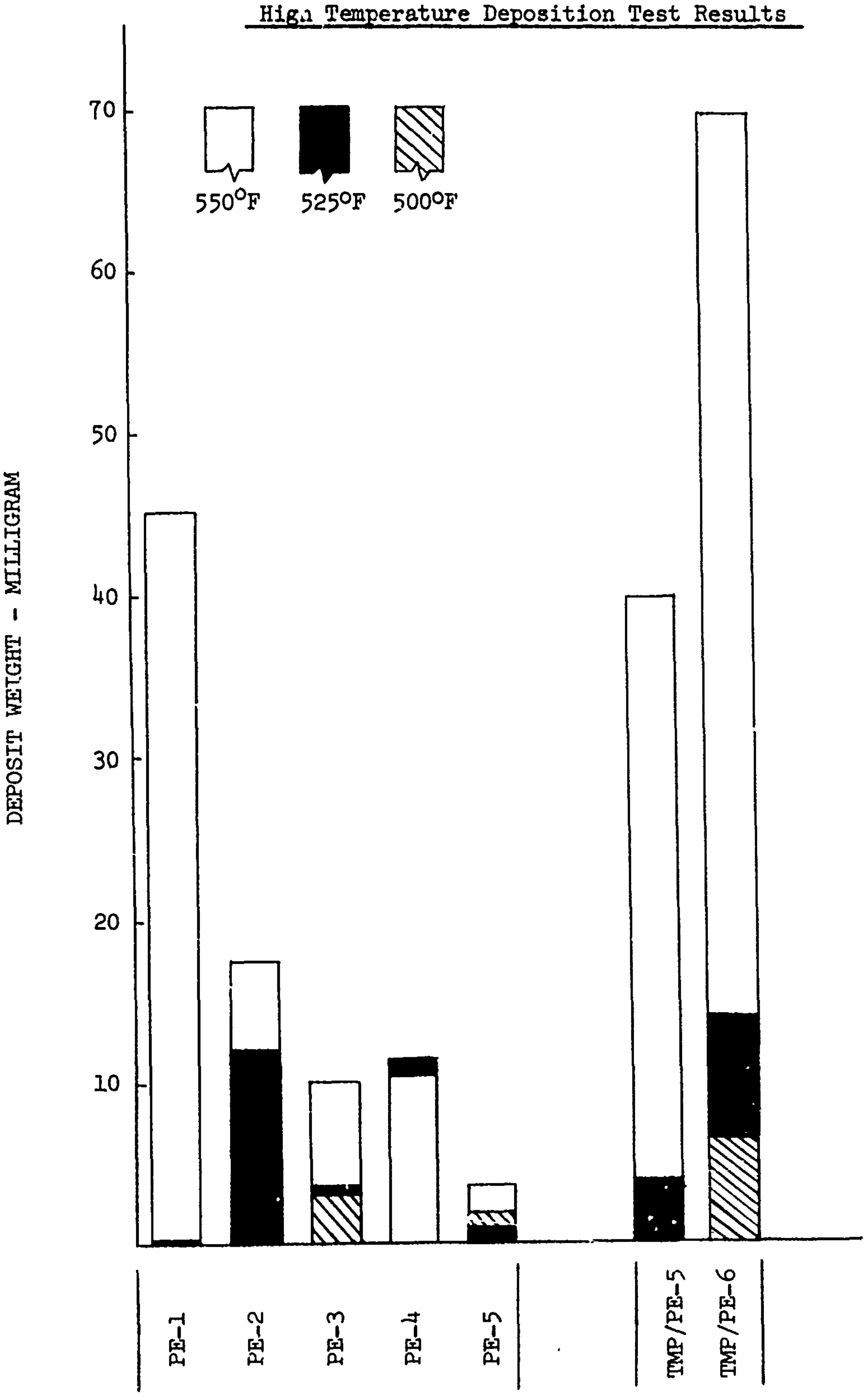


FIGURE 4: BASESTOCK AND ADDITIVE EFFECTS ON VISCOSITY STABILITY

High Temperature Deposition Test Results

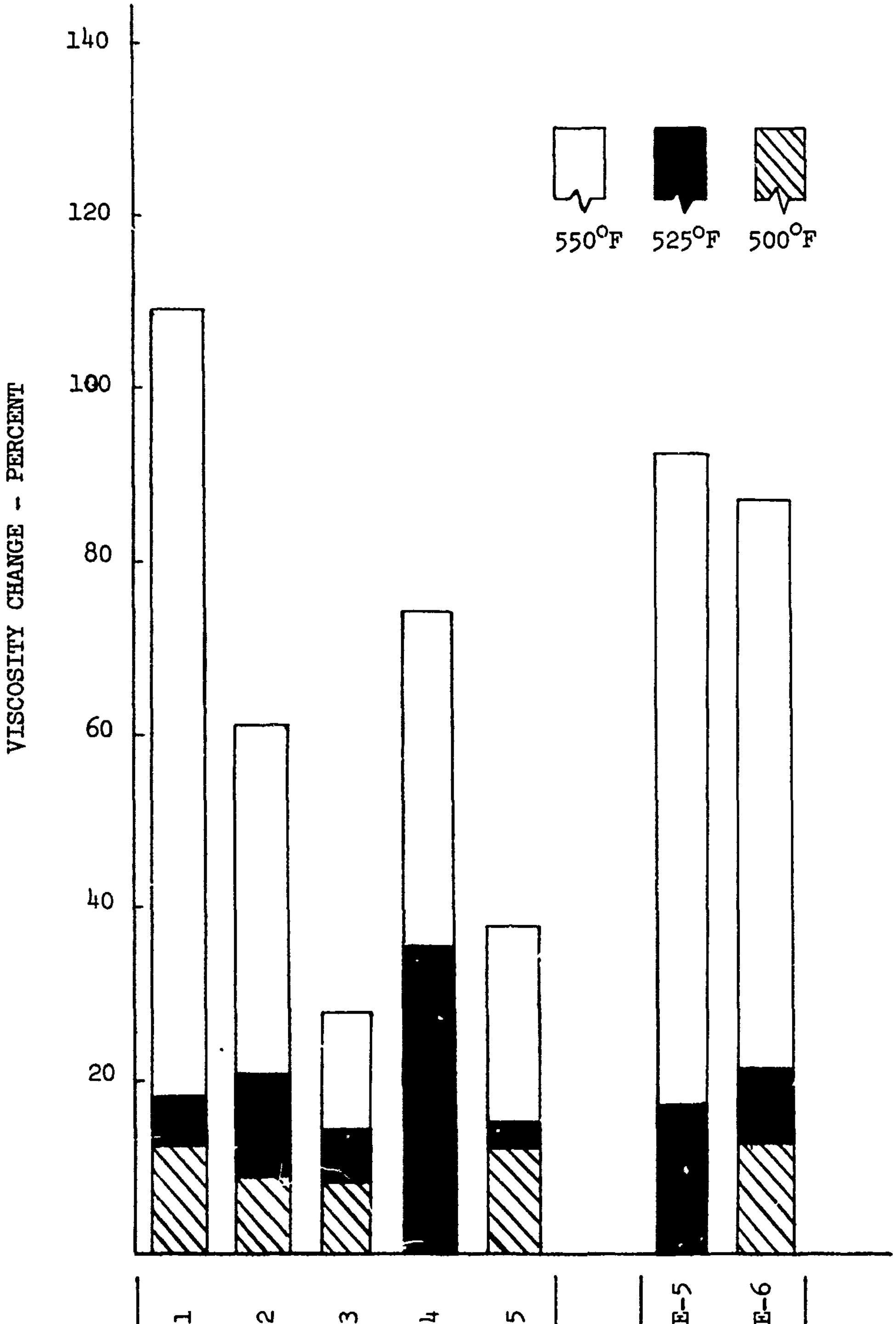


FIGURE 5: BASESTOCK AND ADDITIVE EFFECTS ON TAN

High Temperature Deposition Test Results

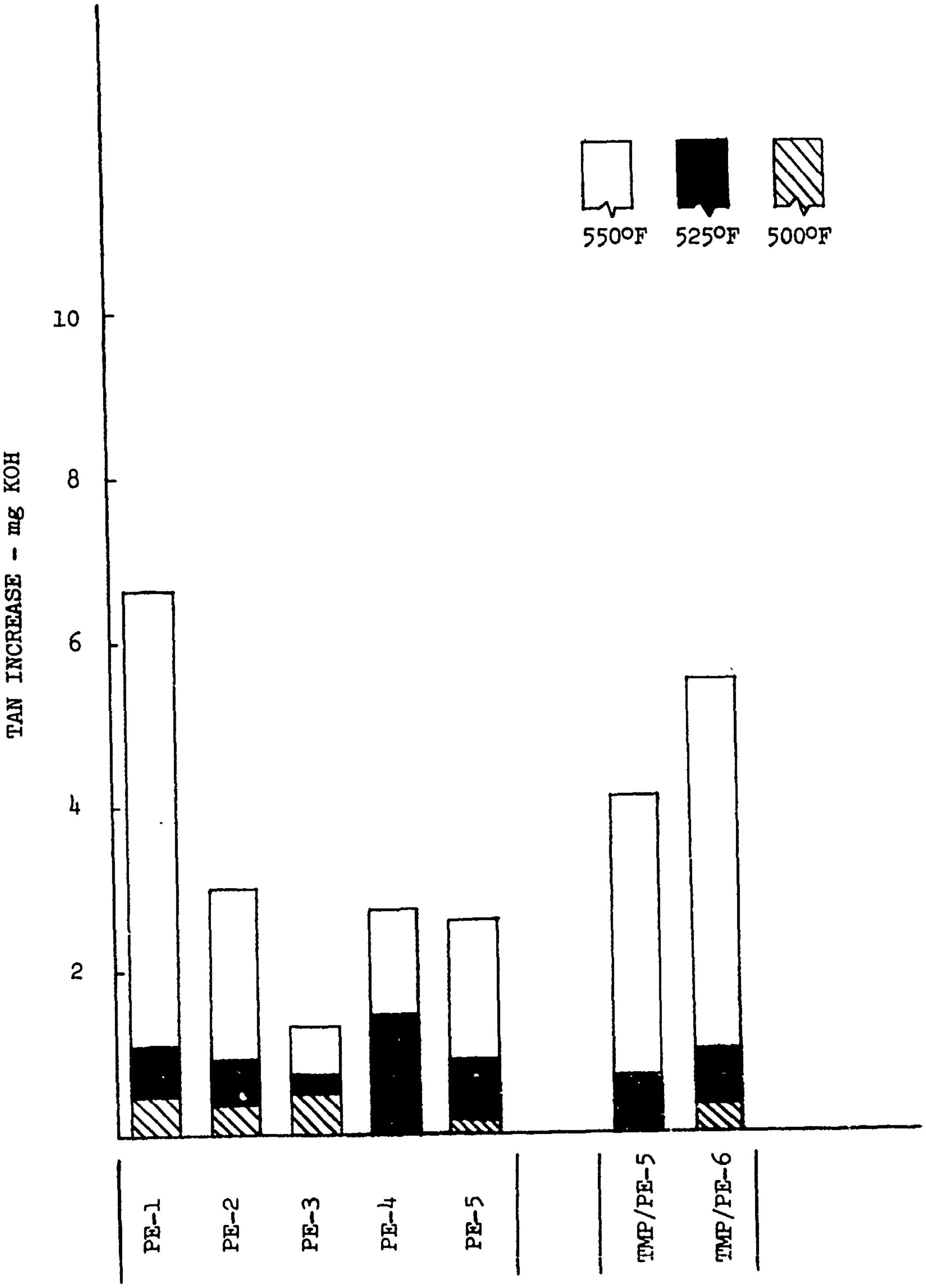


FIGURE 6: BASESTOCK EFFECT ON DEPOSITION CHARACTERISTICS

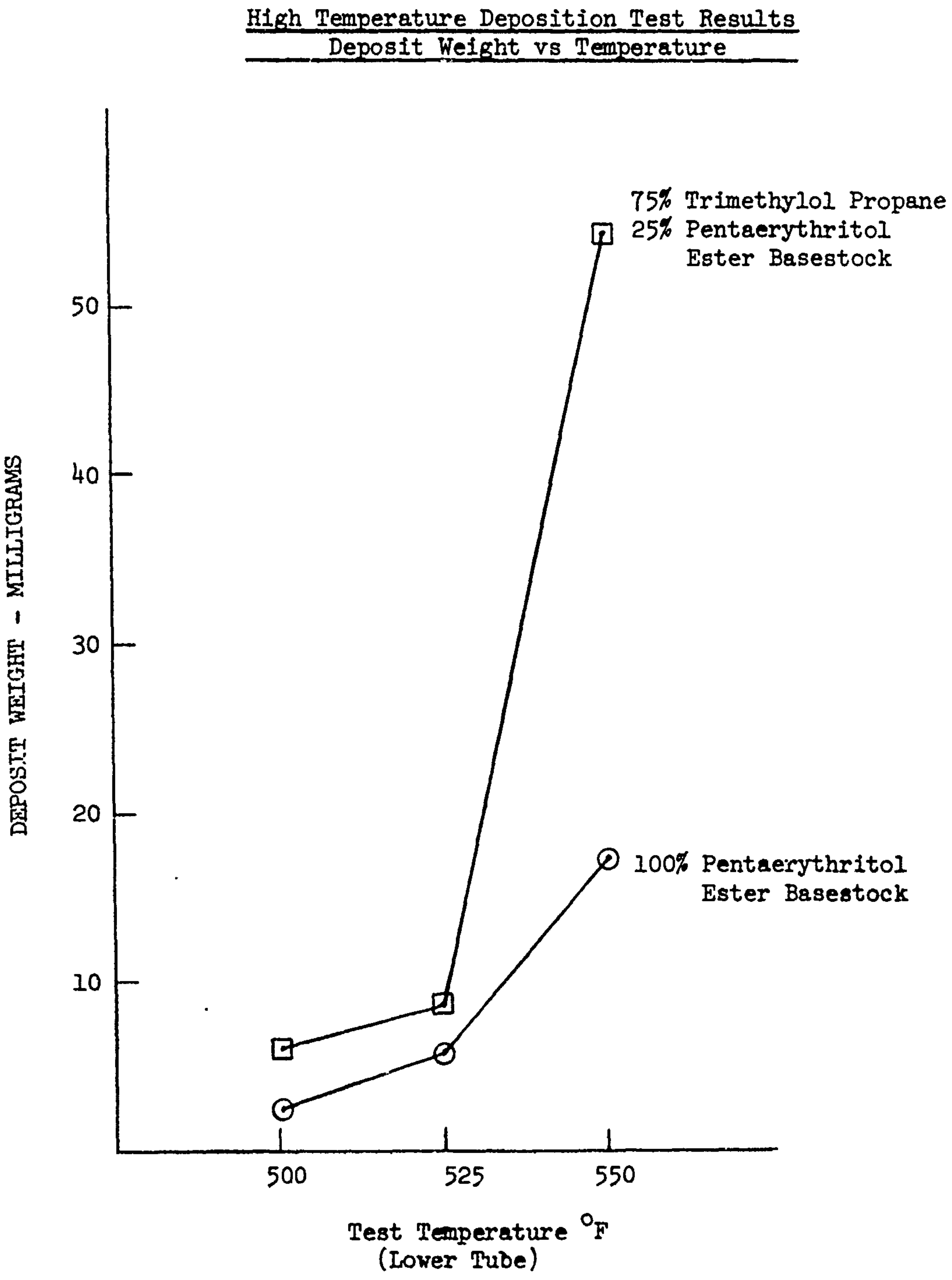


FIGURE 7: BASESTOCK EFFECT ON BULK OIL DEGRADATION CHARACTERISTICS

High Temperature Deposition Test Results
TAN & Viscosity Change vs Temperature

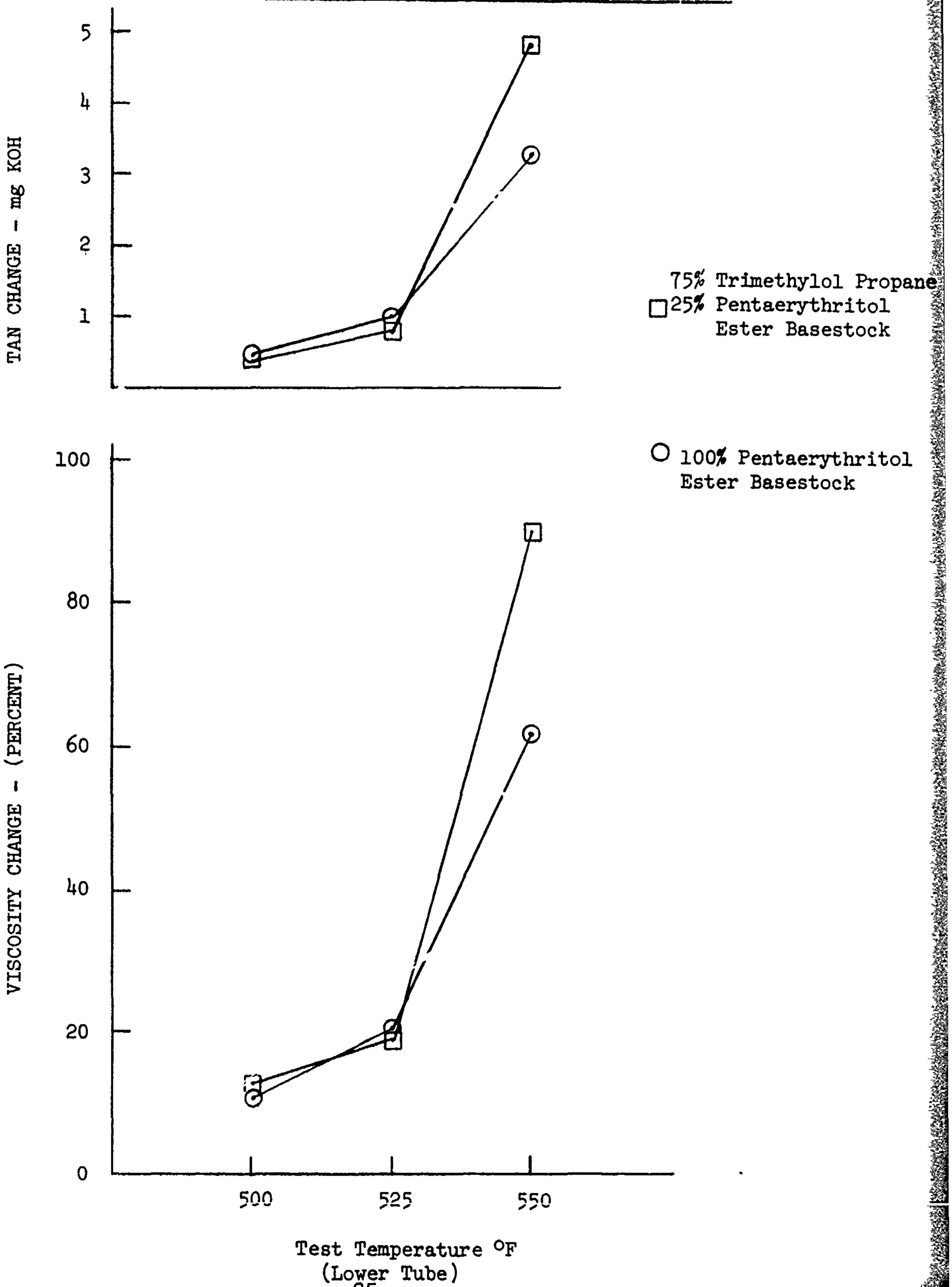


FIGURE 8: COKING CHARACTERISTICS IN NON-OIL WASHED AREAS

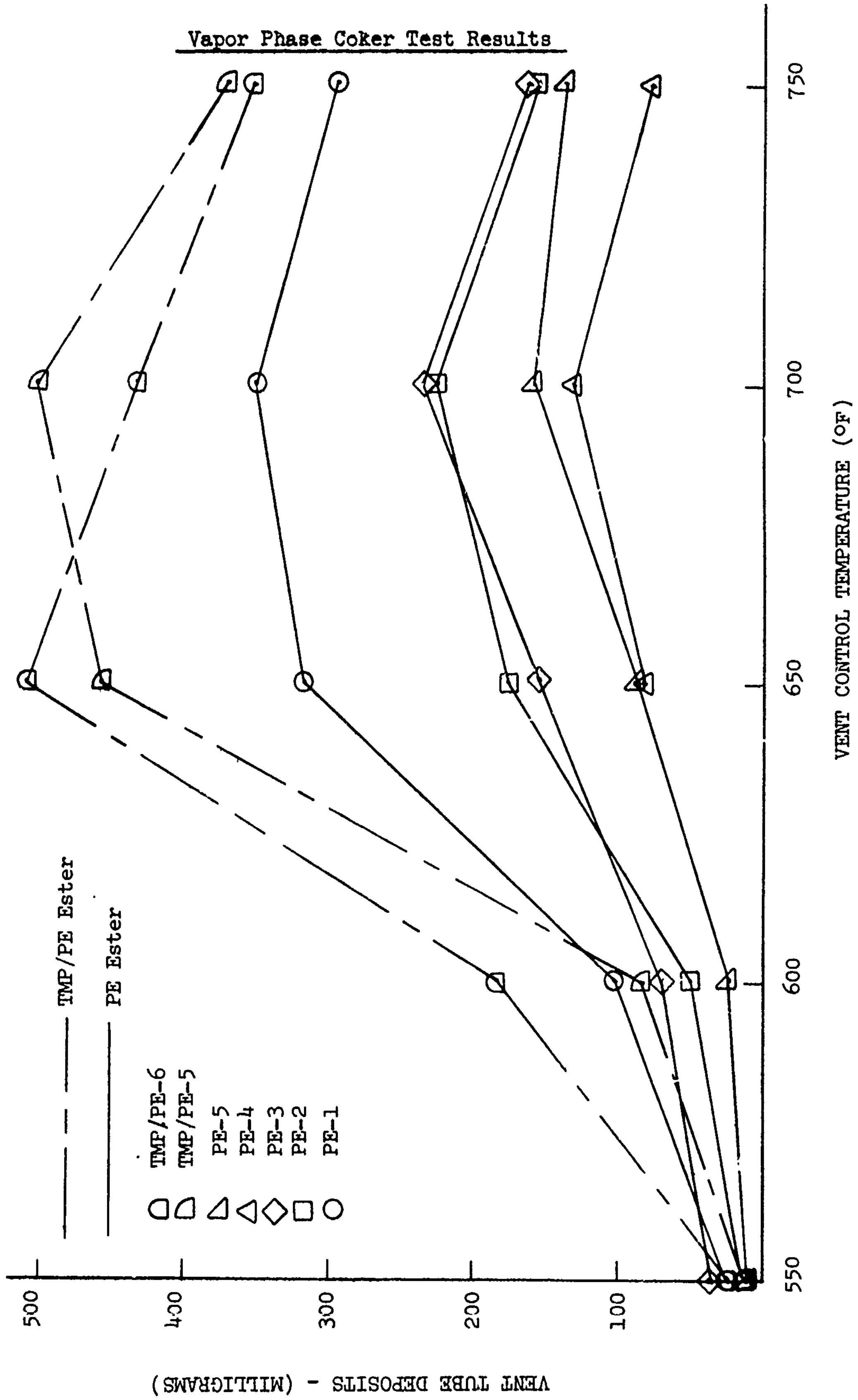
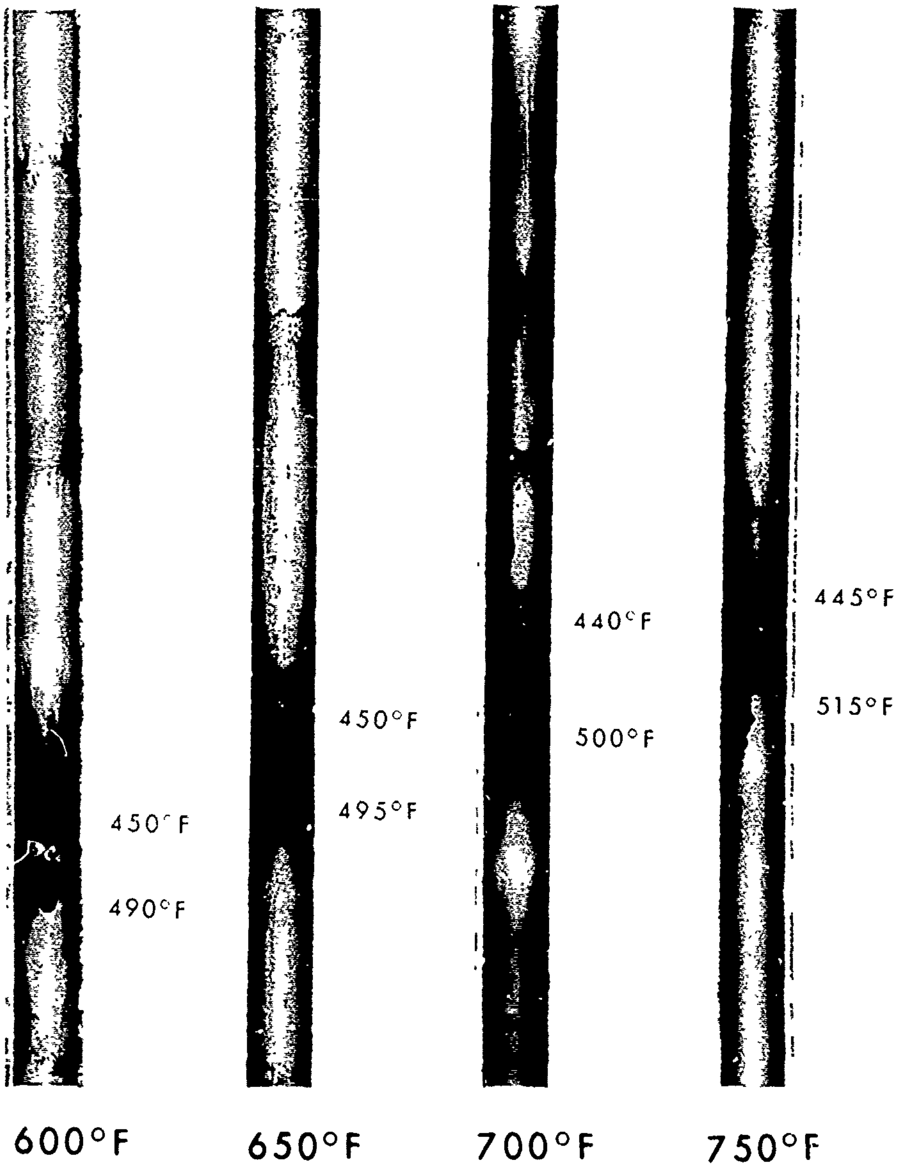


FIGURE 9: DEPOSIT FORMATION IN VENT LINE OF VAPOR PHASE COKER AT VARIOUS VENT CONTROL TEMPERATURES



VENT CONTROL TEMPERATURE

FIGURE 10: DEPOSIT FORMATION IN VENT LINE OF VAPOR PHASE COKER FOR SEVEN MIL-L-23699 LUBRICANTS

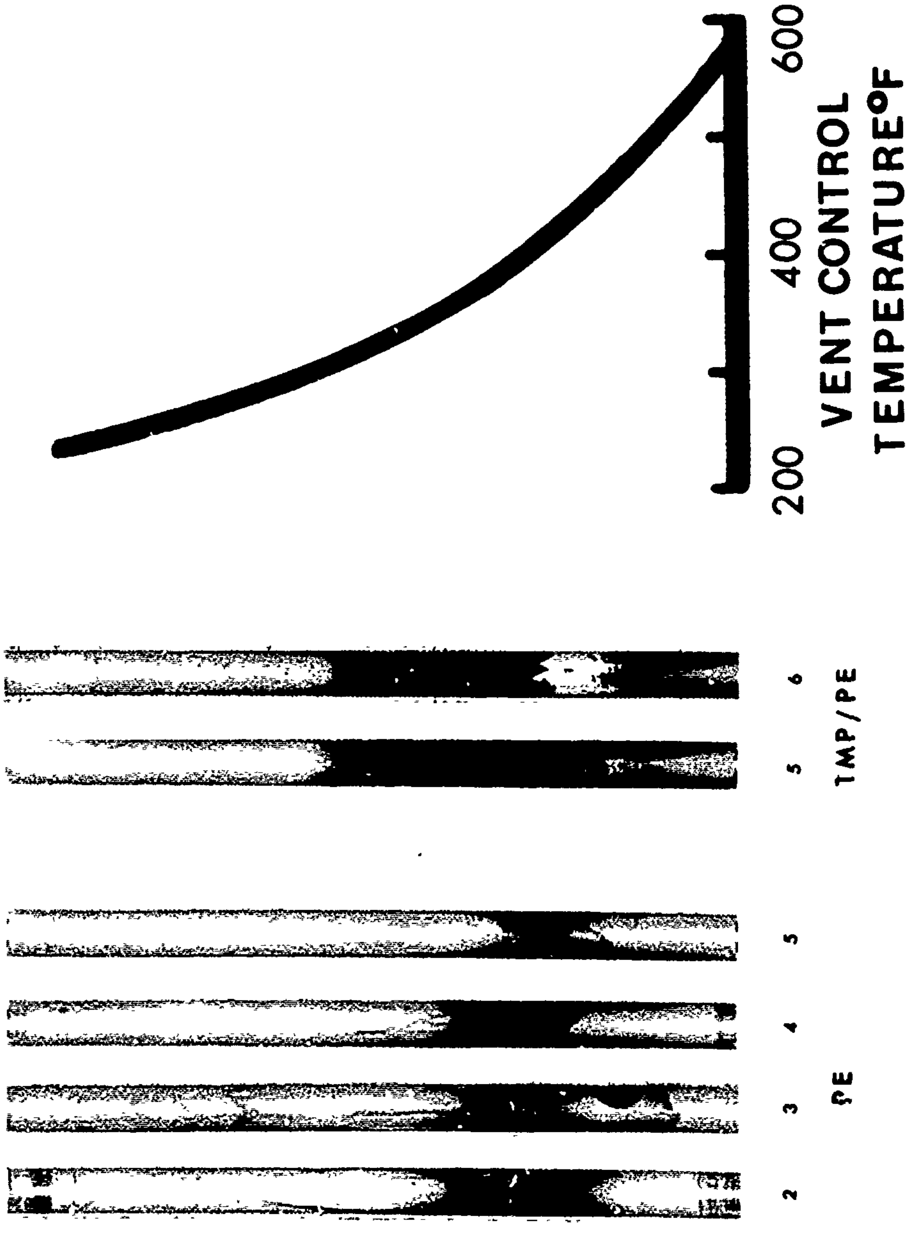


FIGURE 11: DEPOSIT WEIGHTS VERSUS AVERAGE ACID CHAIN LENGTH

Vapor Phase Coker Test Results

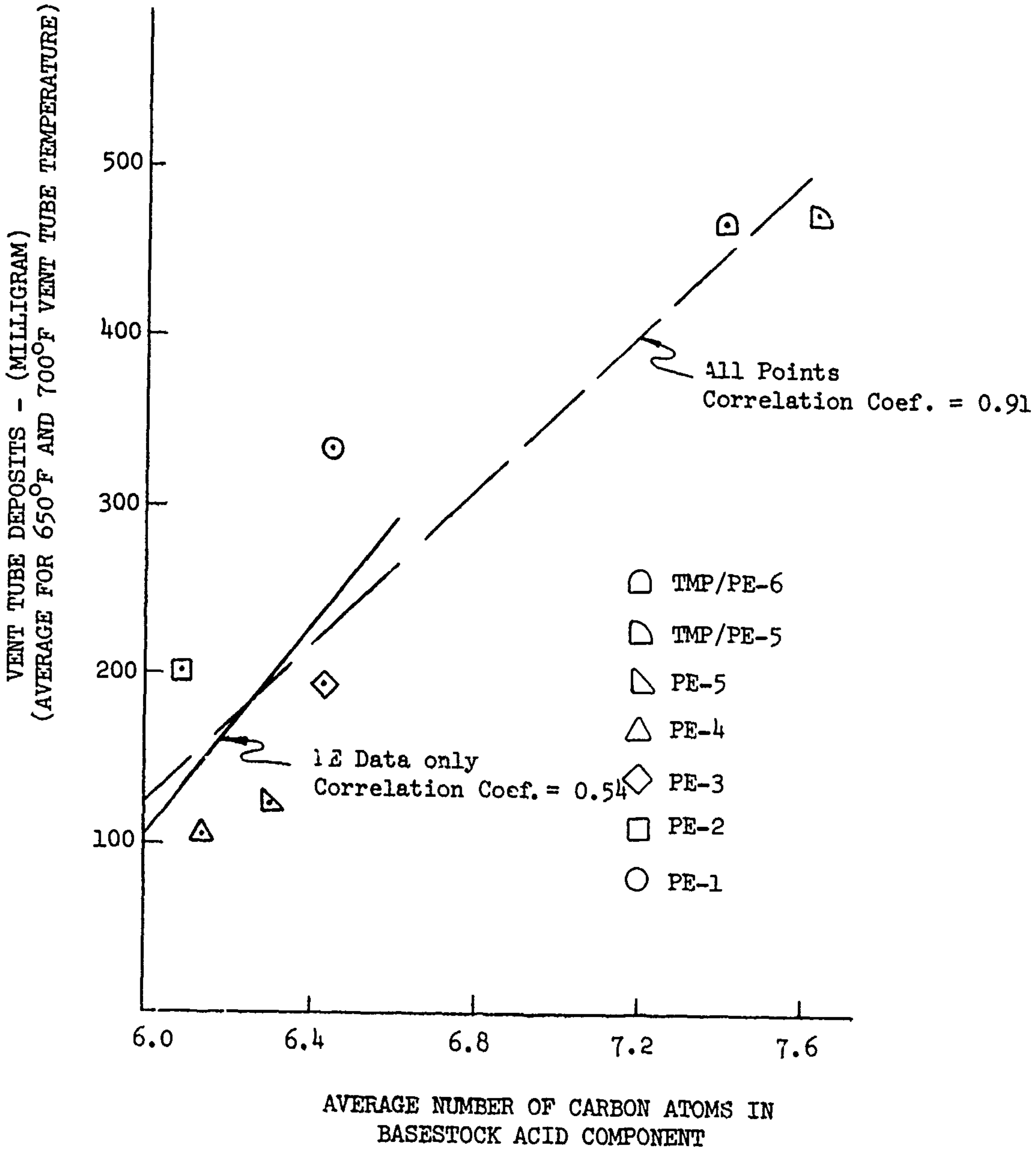


FIGURE 12: DEPOSITS FORMED BY VARIOUS RATIOS OF DIPENTAERYTHRITOL AND TRIMETHYLOL PROPANE ESTER BASESTOCKS

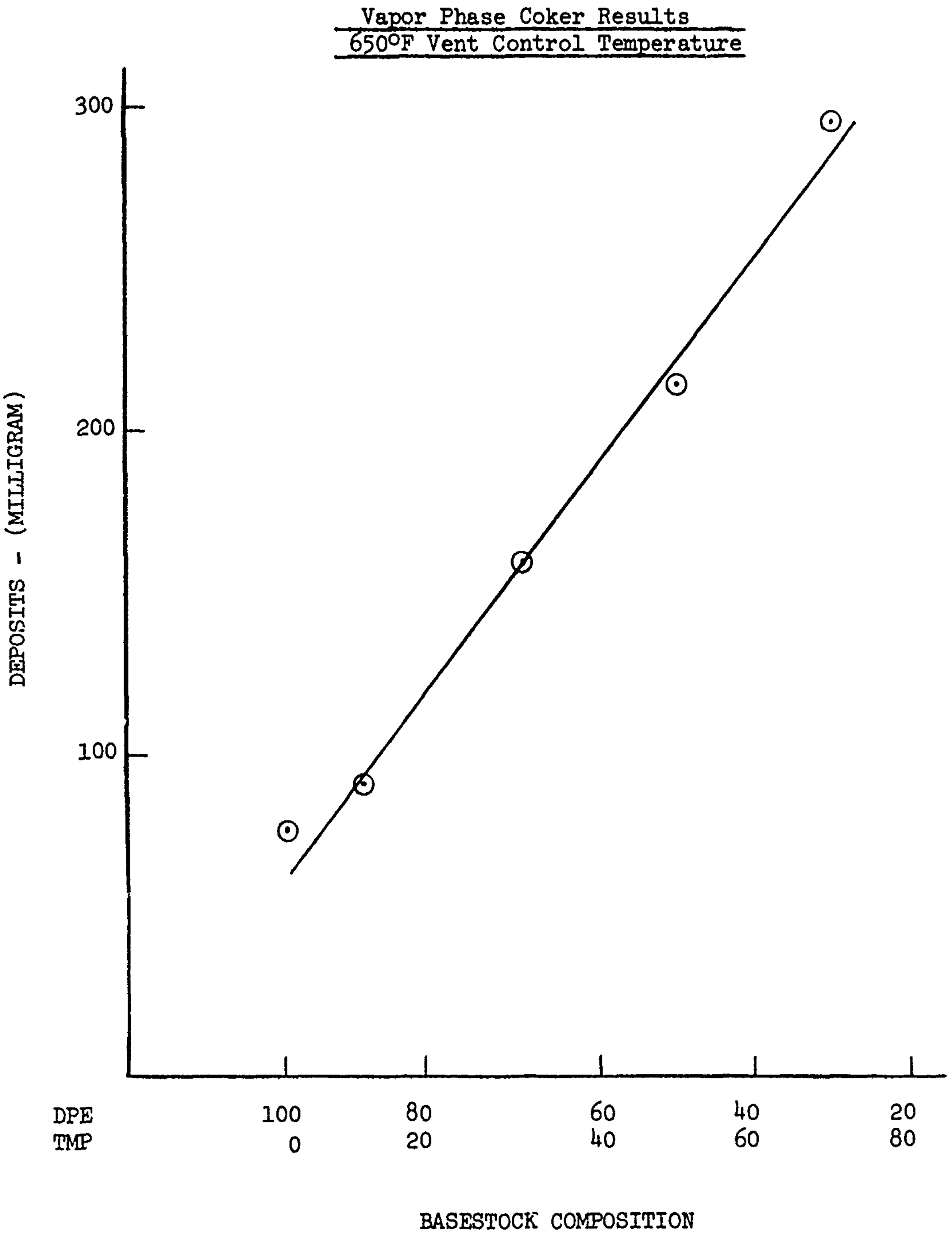


FIGURE 13: YIELD FROM VARIOUS RATIOS OF PENTAERYTHRITOL AND TRIMETHYLOL PROPANE ESTER BASESTOCKS

Vapor Phase Coker Results
650°F Vent Control Temperature

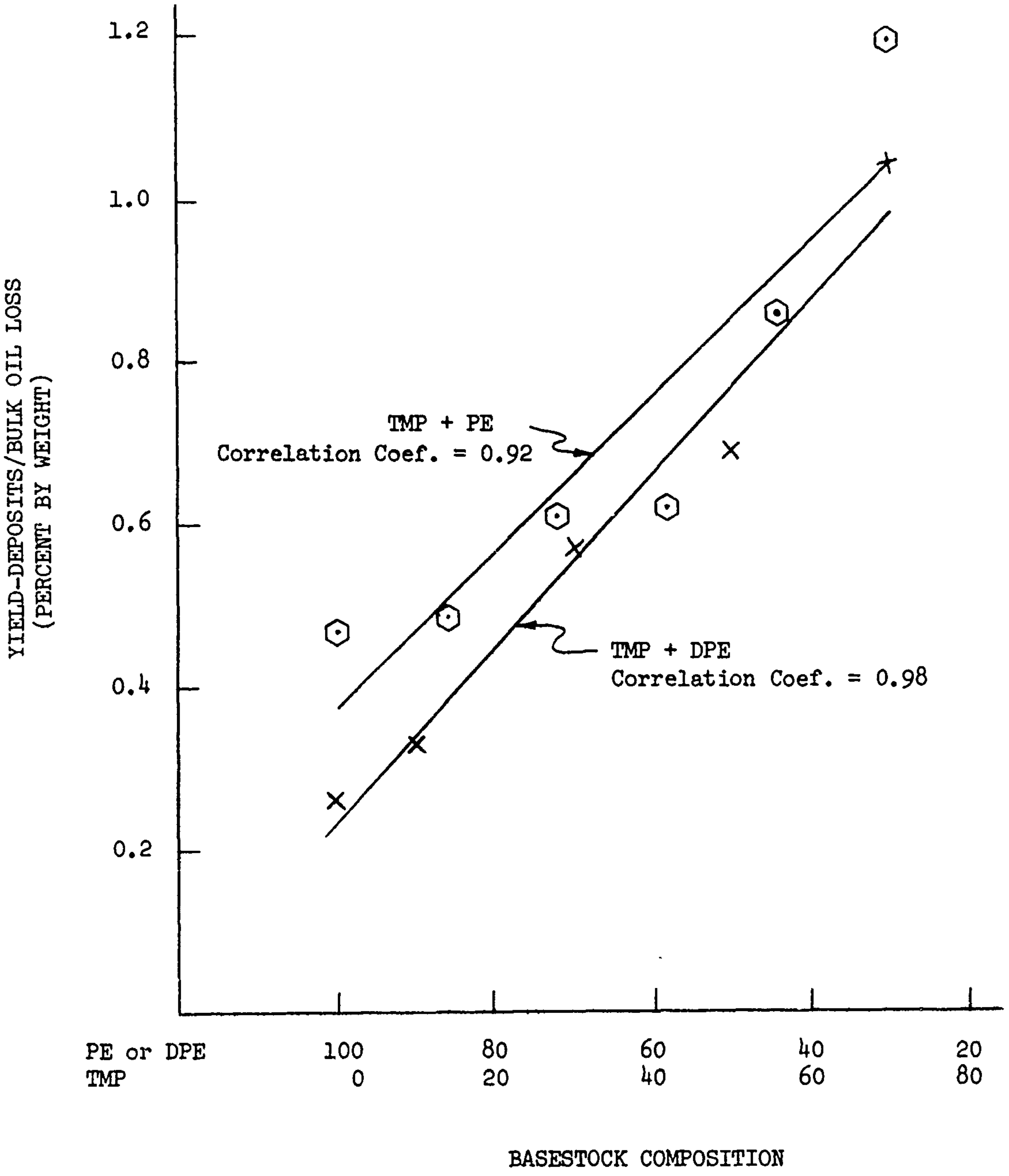


FIGURE 14: YIELD VERSUS AVERAGE ACID CHAIN LENGTH FOR MIXTURES OF PENTAERYTHRITOL AND TRIMETHYLOL PROPANE ESTER BASESTOCKS

Vapor Phase Coker Test Results
650°F Vent Control Temperature

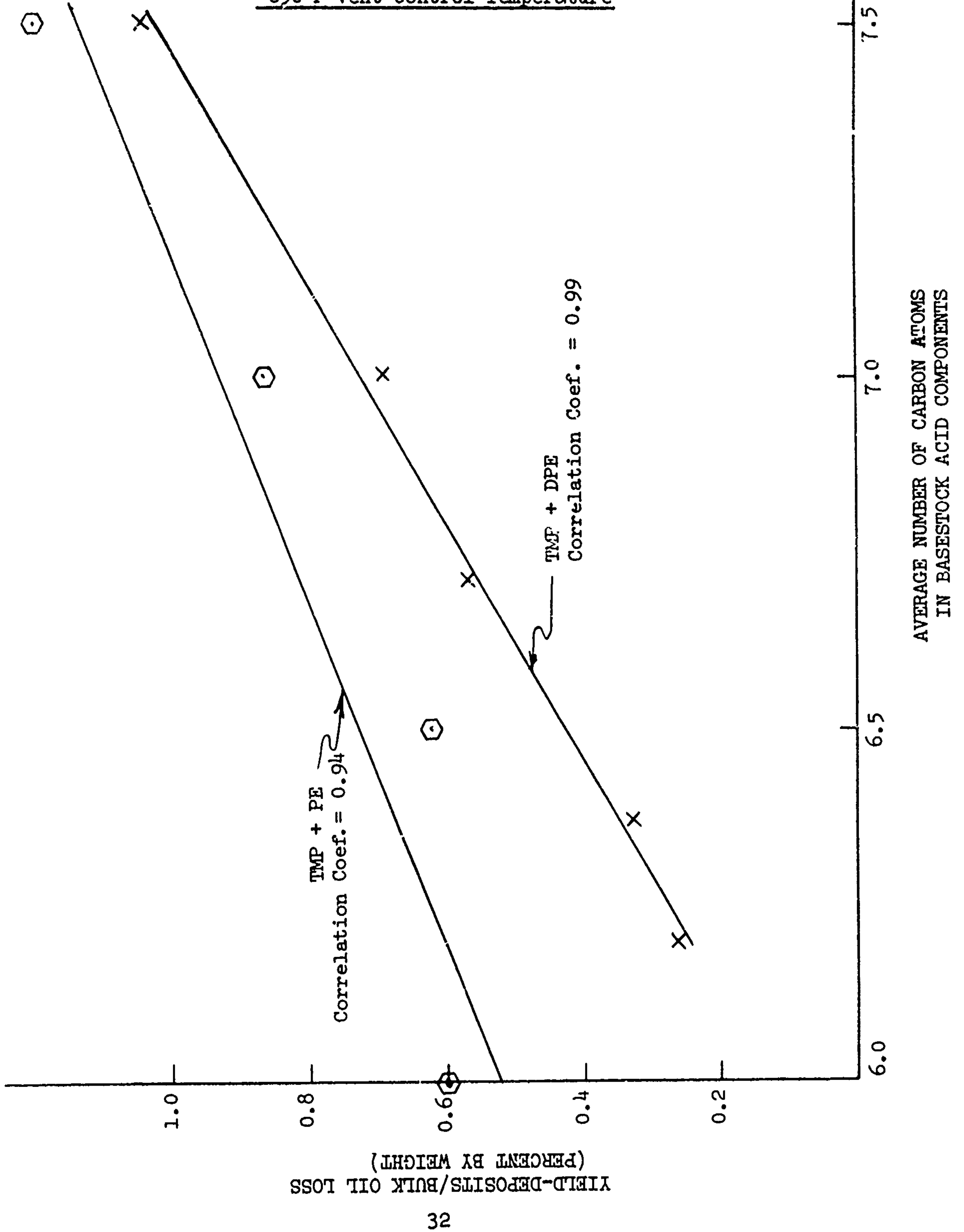
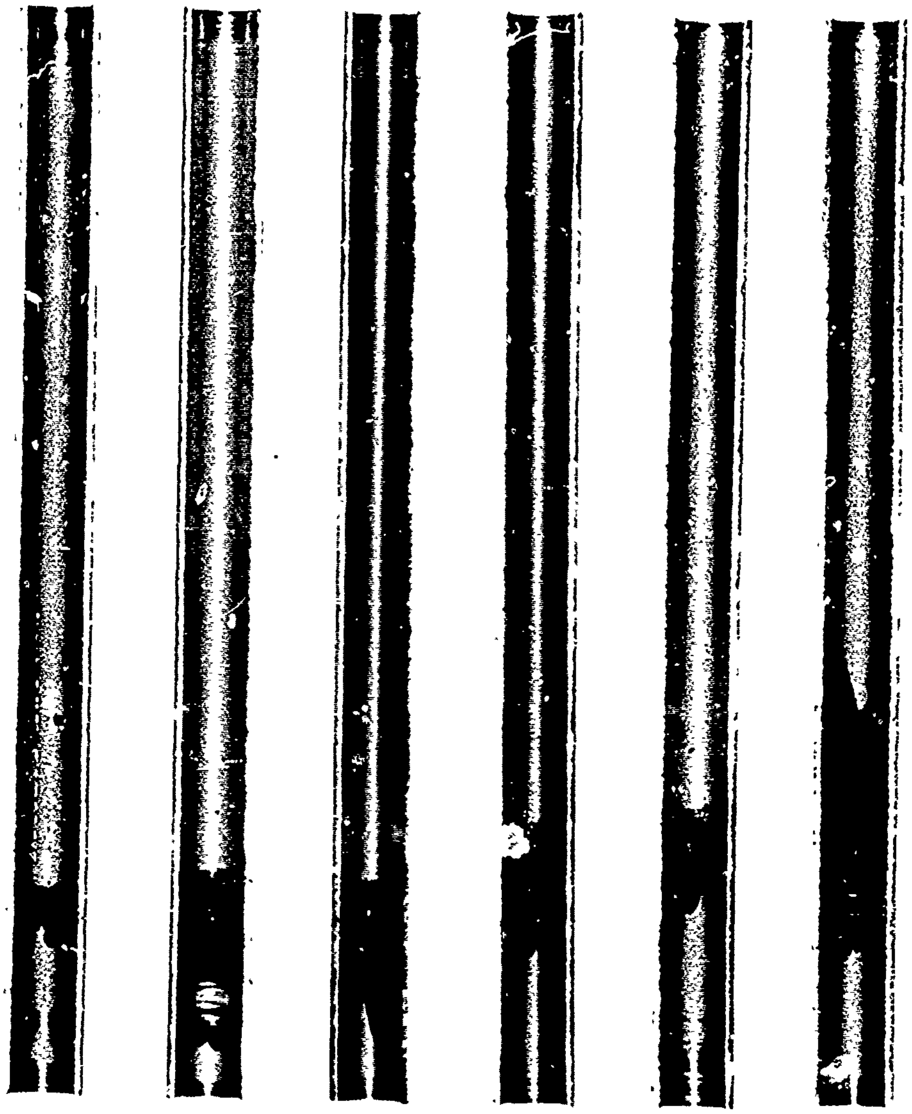


FIGURE 15: DEPOSIT FORMATION IN VENT LINE OF VAPOR PHASE COKER FOR VARIOUS RATIOS OF TMP AND DPE ESTERS

TMP—MIXED ACID ESTER —%	**0**	**10**	**30**	**50**	**70**
DPE—MIXED ($C_{6.2}$) ACID ESTER—%	**100**	**90**	**70**	**50**	**30**

FIGURE 16: DEPOSIT FORMATION IN VENT LINE OF VAPOR PHASE COKER FOR VARIOUS RATIOS OF TMP AND PE ESTERS



TMP—% (MIXED ACID ESTER)	0	14	28	42	56	70
PE—% (SINGLE, C_5, ACID ESTER)	100	86	72	58	44	30

FIGURE 17: YIELD VERSUS AVERAGE ACID CHAIN LENGTH FOR ESTERS OF PENTAERYTHRITOL AND TRIMETHYLOL PROPANE

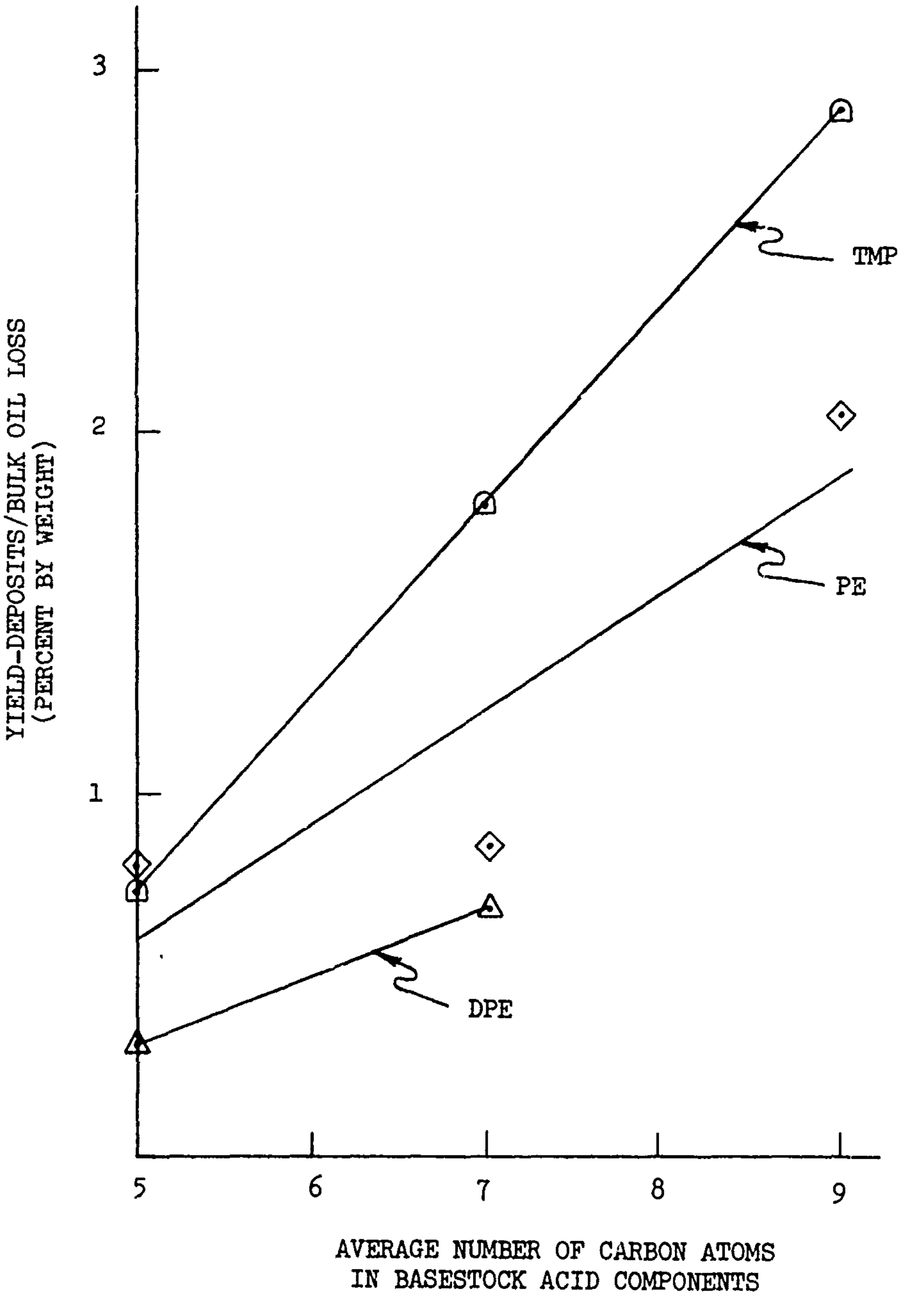


FIGURE 18: DEPOSIT FORMATION IN VENT LINE OF VAPOR PHASE COKER FOR VARIOUS ALCOHOL-ACID COMBINATIONS OF THE BASE ESTER

FIGURE 19: TEMPERATURE AT LOCATION OF MAXIMUM DEPOSIT DENSITY FOR VARIOUS ACID CHAIN LENGTHS OF THE BASESTOCK ACID COMPONENT

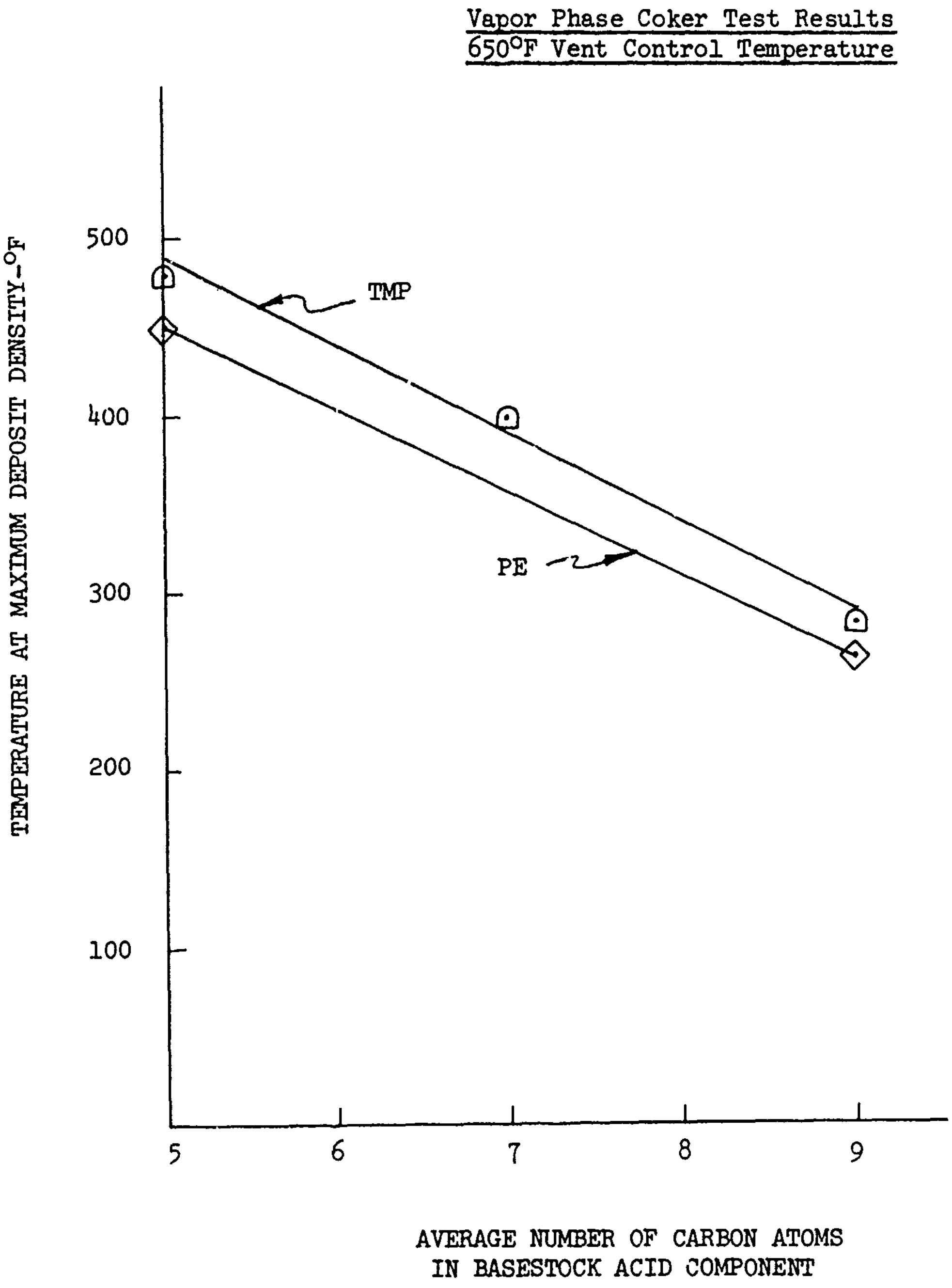


FIGURE 20: DEPOSITION REGION RELATED TO CHAIN LENGTH OF THE ACID COMPONENT OF ESTER BASESTOCKS

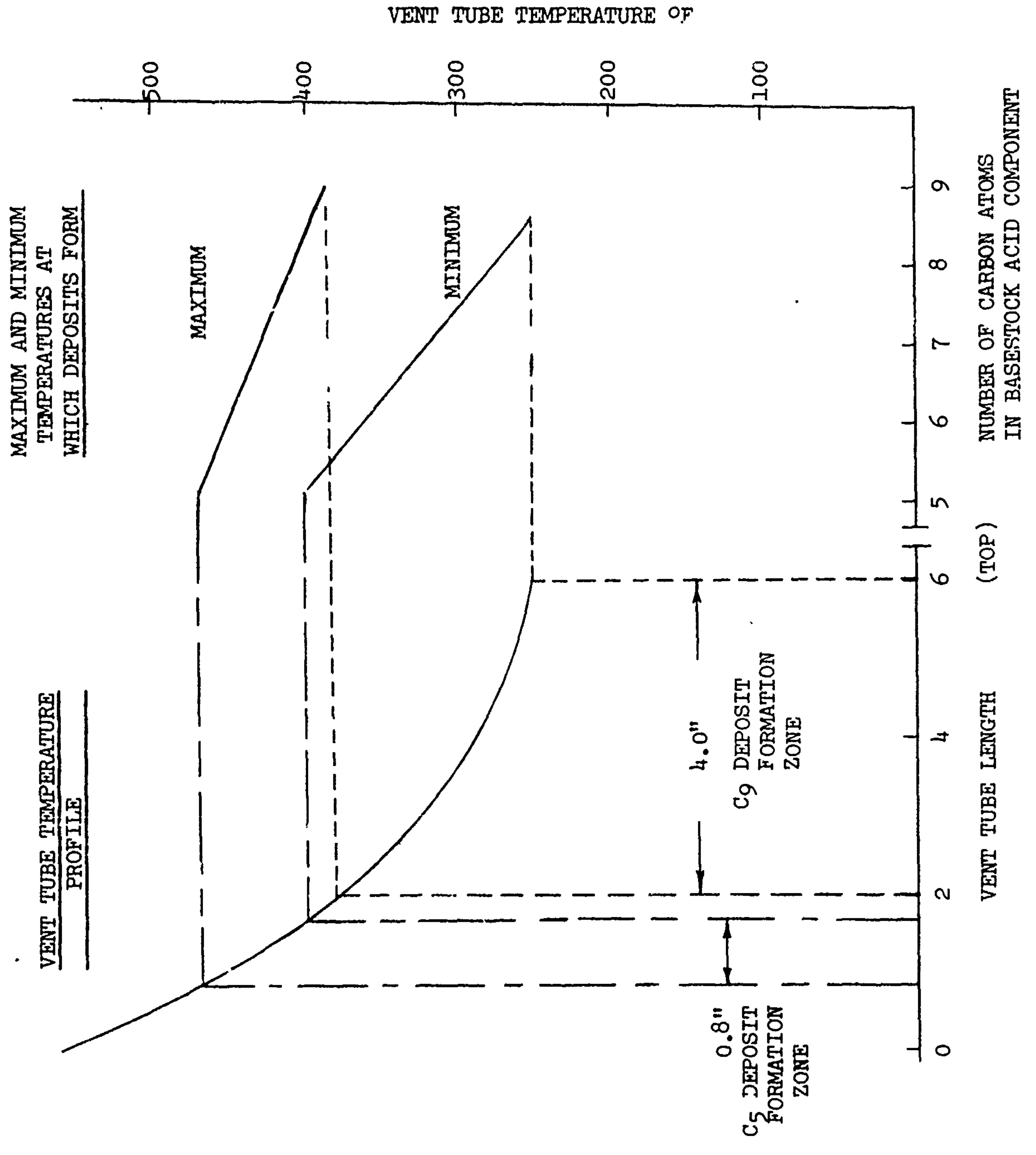
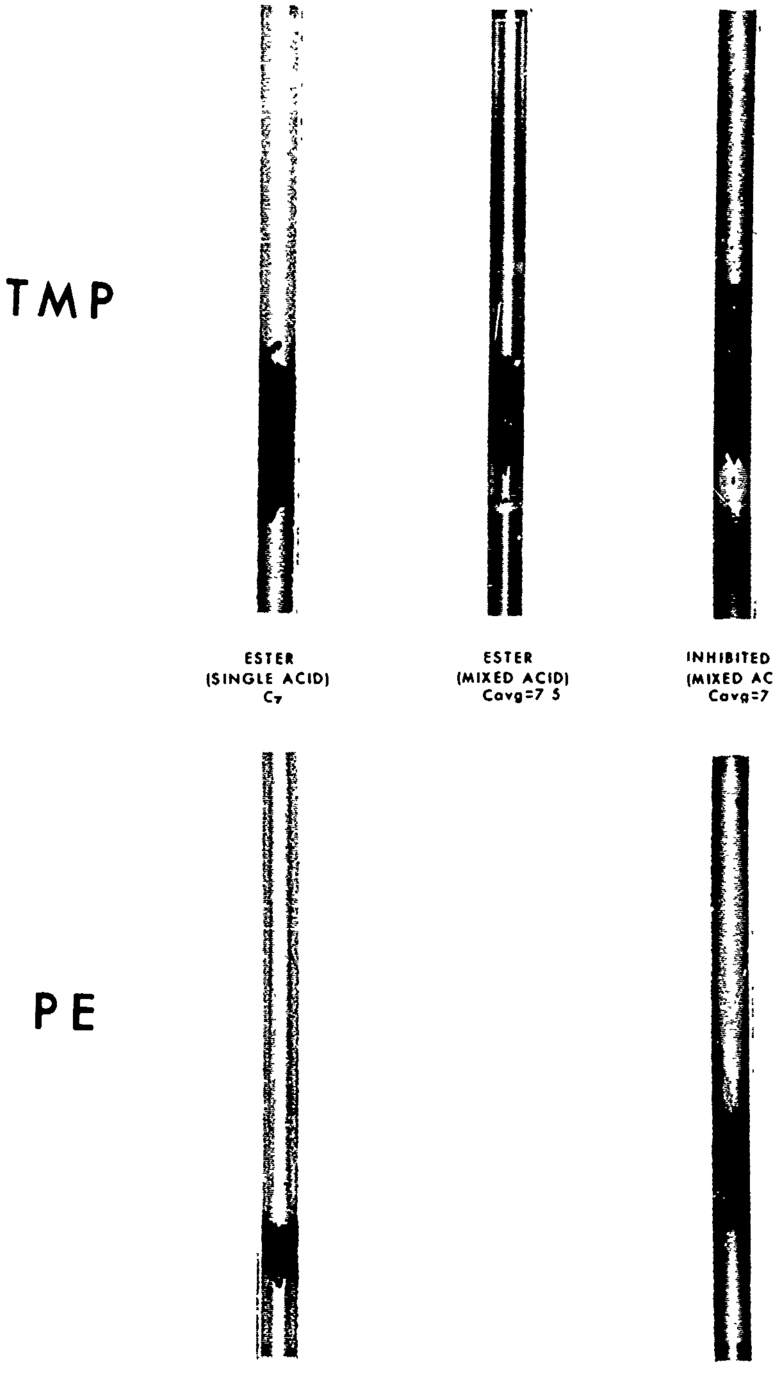


FIGURE 21: DEPOSIT FORMING PATTERNS AS RELATED TO ACID CHAIN LENGTHS



ESTER (SINGLE ACID) C_7

ESTER (MIXED ACID) Cavg=7.5

INHIBITED OIL (MIXED ACID) Cavg=7.5

ESTER (SINGLE ACID) C_5

INHIBITED OIL (MIXED ACID) Cavg= 6.1

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7. WORK UNIT ASSIGNMENT - NAPTC-316-5R6-1-13, Analysis of Service Performance of Lubricating Oils, 28 June 1971

APPENDIX A

OPERATING PROCEDURE FOR VAPOR PHASE COKER

INTRODUCTION

The Vapor Phase Coker consists essentially of a three neck flask (oil reservoir) surrounded by an electric heating mantle, an intermediate "heating" tube surrounded by a coiled rod type heater, and a steel "breather" tube on which the deposits are formed. See Figure A-1

In operation, air is fed through a tube entering one neck of the flask, bubbled through the oil and permitted to escape through the center neck of the flask. Upon leaving the flask the vapors pass through the heater tube and then directly into the coking "breather" tube, where the deposits are formed. A typical vent tube temperature profile is shown in Figure A-II.

A thermocouple is inserted through the third neck of the flask and immersed in the oil for monitoring and controlling oil temperature. A second thermocouple is located in the heater section.

The capacity of the oil reservoir flask is 2000 ml. The coker tube is 6 inches long, 0.500 inch on the outside diameter with a 0.049 inch wall thickness.

PREPARATION

Coker Tube

The preparation procedure is as follows:

1. Rinse the tube in SD-1 solvent and wipe dry with a lint-free cloth. Wash down with acetone and allow to dry.

2. Place the coker tube in a clean storage tube fitted with a vented stopper and labeled with the serial number of the tube.

3. Place the test tube containing the coker tube in a 220°F oven for ½ hour.

4. After coker tube is cooled to room temperature weigh to the nearest 0.001 gram. Record the weight on a tube inventory list and on the storage tube label.

5. Return coker tube to storage tube fitted with a solid stopper and store until needed.

Test

1. Connect vapor phase coking tube to vent heater assembly. Tighten nut to 250 in-lb.

2. Place insulation around vapor phase coking tube and secure with wire. Place draft shield over insulation and vent tube.

3. Pour 900 ml of test fluid into flask.

4. Weigh flask with test fluid to nearest hundredth of a gram. Record on data sheet.

5. Place flask with test charge in mantle and zip mantle shut.

6. Position mantle and flask on insulation pad and connect mantle power sources.

7. Insert air-inlet stopper and thermocouple (T/C) in glass stopper into outside flask necks. Connect air line to air-inlet tube and position tip of T/C so that it is located approximately one inch from the bottom of the flask.

8. Insert end of vent heater assembly with teflon stopper through heater support and then into center neck of flask.

9. Connect power source to heater terminals.

10. Connect T/C lead from heater section to T/C block.

TEST - STANDARD

Conditions

Bulk Oil Temp. (Sump)	400°F
Tube Heater Temperature	Variable
Air Flow	0.027 scfm (dry air)
Time	17 hours

Test Sequence

1. Adjust air supply to rotometer to 20 psi, then adjust air flow to 50 percent of maximum air flow on cabinet rotometer. (This adjustment allows an air flow of 0.027 scfm).

2. Turn on cabinet power switch.

3. Adjust vent heater variac to obtain 120 volts.

4. Set flask (bulk oil) temperature controller to 400°F.

5. When vent temperature reaches approximately 100°F below test temperature, reduce voltage to approximately 30 volts.

6. Make necessary adjustments to stabilize test conditions.

7. Take and record bulk oil temperature, tube heater temperature and air flow at one hour intervals.

8. At the end of 17 hours running time, turn off power switch, shut off air flow and allow to cool down.

9. Weigh flask with test fluid to nearest hundredth of a gram. Record on data sheet.

PROCEDURE FOR DETERMINING DEPOSIT WEIGHTS

1. Remove vapor phase coking tube from heater assembly.

2. Remove nut and ferrule from tube.

3. Fill a test tube with stoddard solvent and insert vapor phase coking tube. Soak for one hour. Remove from test tube and allow solvent to drain off.

4. Place in clean dry storage tube and put in a 200°F oven for one hour.

5. When cool, weigh coker tube to nearest milligram.

6. Record gross weight - determine deposit weight by subtracting tare weight of tube. Record deposit weight.

7. After review of results have the tube split lengthwise to examine deposits.

POST TEST CLEANING PROCEDURES

1. Flask

Drain flask into a clean one quart sample bottle. Label bottle with lube oil code number, test number, and date of test.

Examine empty flask for deposits remaining in flask.

Wash with acid dichromate solution. Rinse with distilled water. Final rinse with acetone and allow to dry.

2. Heater Section

Wire brush inside of tube with SD-1 solvent. Follow with acetone rinse.

3. Wash air inlet tube and thermocouple with SD-1 solvent. Follow with acetone rinse.

FIGURE A-I: VAPOR PHASE COKER TEST SECTION SCHEMATIC

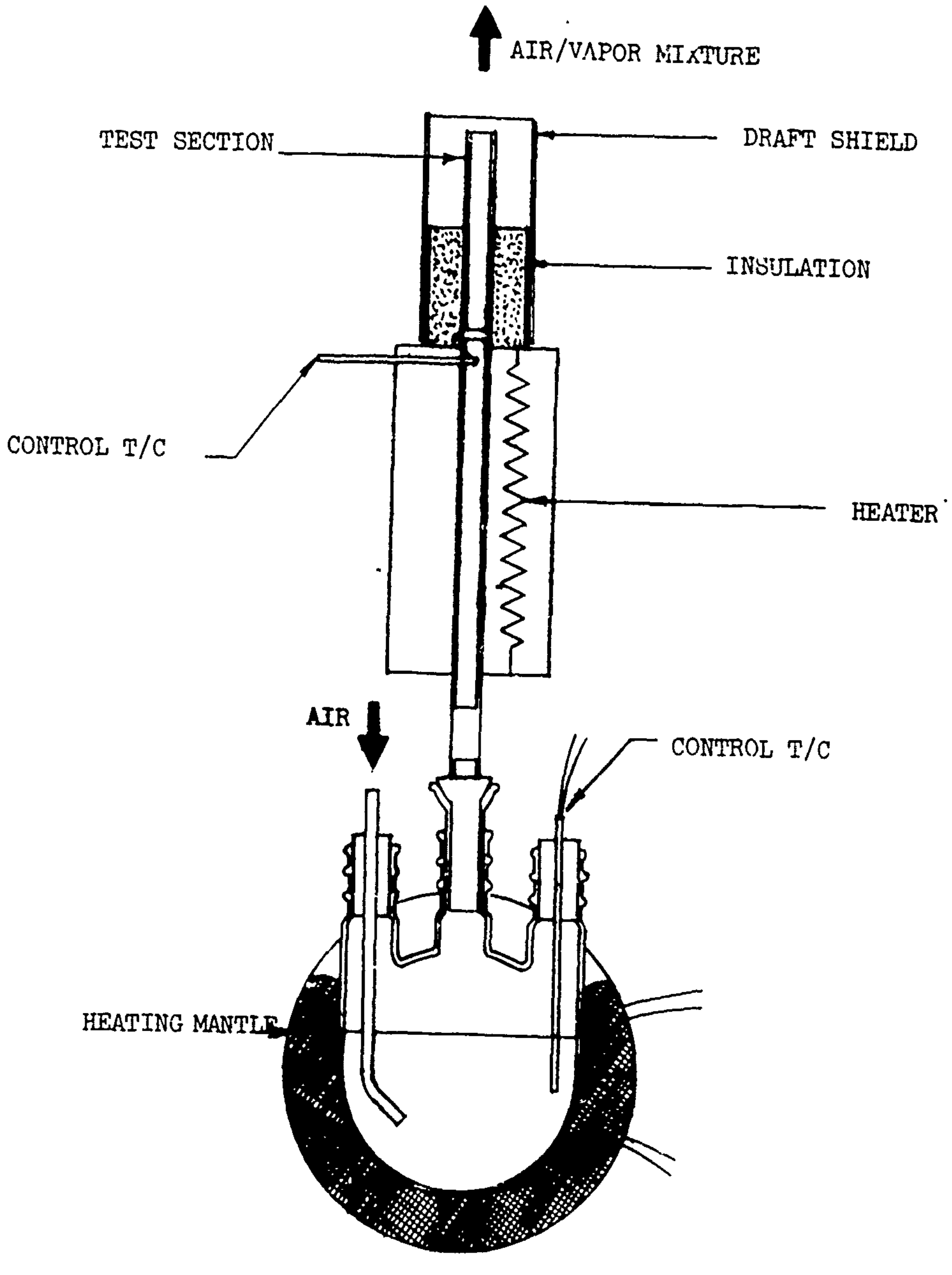
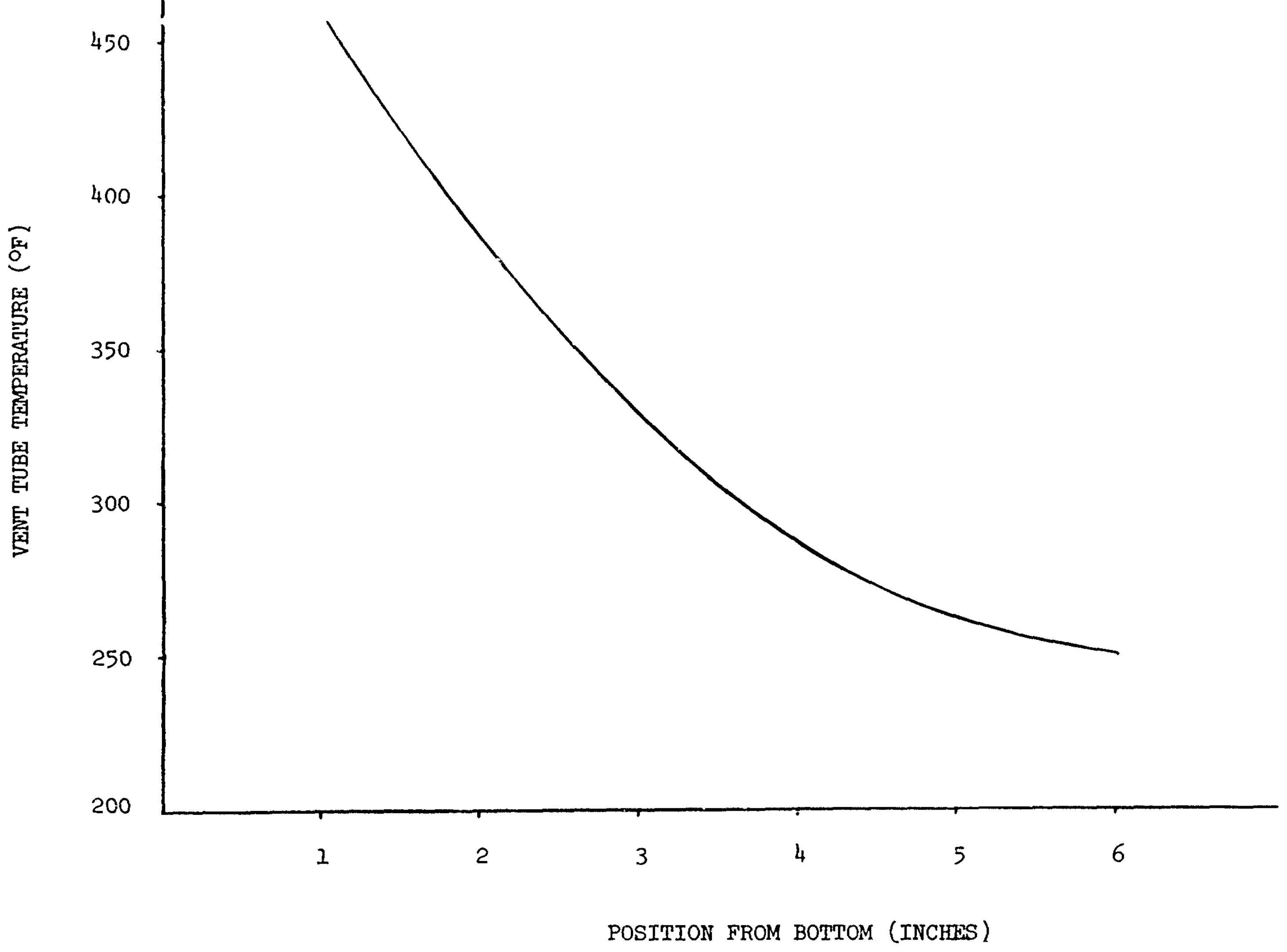


FIGURE A-II: VAPOR PHASE COKER
VENT TUBE TEMPERATURE PROFILE
(650°F CONTROL TEMPERATURE)



APPENDIX B

HIGH TEMPERATURE DEPOSITION TEST RESULTS AND ANALYSIS

High Temperature Deposition (HTD) Tests were run on several lubricants at three temperature levels at the lower section of the deposition tube. The results of these tests are summarized in Tables B-I, B-II, B-III.

The results of Tables B-I, B-II, B-III are plotted and discussed in the main text. The differences in mean values at 500 and 525°F between PE and TMP/PE esters for deposits, viscosity change, and TAN change were considered too small to warrant statistical analysis to examine for significance. However, the results shown in Table B-III (for lower tube temperature of 550°F) were statistically analyzed to determine the significance of the differences that are apparent between PE and TMP/PE esters with regard to deposits formed, viscosity change and TAN change. The analysis provides a means of distinguishing between differences that are real, i.e. attributable to the two basestocks, or the result of experimental error.

In the computations all factors except basestock variation (PE vs TMP/PE) were ignored. Additive effects (e.g. PE1 vs PE2 etc.) as well as the duplication of tests on formulations were treated as contributing to experimental error. The analysis simply compared the mean values of PE vs TMP/PE and provided the information necessary to make judgements on the reality of observed differences based on the probability of either experimental error or chance contributing to the differences.

The results of the statistical analysis are given in Table B-IV. The method of analysis consisted of applying the "t" test for the comparison of two randomized groups with unequal numbers of samples. This method is described in detail in reference 1 of this Appendix.

The first step was to calculate the means and standard deviations for each of the two groups (PE and TMP/PE) of data for each property (deposits, Δ viscosity and Δ TAN). These statistics are given in Table B-IV for each group. Since the computation of "t" is dependent upon the equality or inequality of the standard deviation, the next step was to perform an "F" test on the standard deviations in order to make judgements concerning their equality between the groups. The "F" values are also shown in Table B-IV. The calculated "F" values, when compared to the 5 percent level distribution of "F", (reference 1) show that the standard deviation between both groups for all three properties can be considered equal.

The next step was to calculate the "t" values for randomized groups having equal standard deviations. These "t" values along with a comparison to values from the distribution of "t" at specific probability levels are also shown in Table B-IV. These results show that there is only about a 1 in 100 probability that the difference in the means for deposits formed by PE and TMP/PE are caused by experimental error or chance. They also show that, for Δ viscosity and Δ TAN, the differences in the mean values between groups could occur about 1 out of every 5 times as a result of error or chance.

Therefore, the conclusions drawn from this statistical analysis are that, in the 550°F HTD test, PE and TMP/PE esters possess different deposit forming tendencies, but no distinction can be made in their ability to resist change in viscosity or TAN.

References

1. Text - Snedec , G.W., "Statistical Methods";, The Iowa State University Press, Ames, Iowa 1956.

TABLE B-I

HIGH TEMPERATURE DEPOSITION TEST RESULTS
500°F LOWER TUBE TEMPERATURE

FORMULATION	NAPTC CODE	DEPOSIT (mg)	VISCOSITY (100°F) @ 48 HRS (cs)	VISCOSITY CHANGE %	TAN @ 48 HRS (mg KOH)	TAN CHANGE (mg KOH)
PE1	L283	0	30.89	12.6	0.60	0.58
		0	30.72	12.0	0.39	0.37
PE2	L214	0	29.67	8.3	0.53	0.51
		0	29.72	8.5	0.34	0.32
PE3	L360	3	29.07	8.3	0.95	0.55
		-	-	-	-	-
PE4	-	-	-	-	-	-
PE5	L340	2	31.54	12.0	0.23	0.20
PE (Mean)		0.3	30.3	10.3	0.51	0.42
TMP/PE5		-	-	-	-	-
TMP/PE6	L296	6	29.30	13.5	0.52	0.27
		6	28.86	11.8	0.79	0.54
TMP/PE (Mean)		6.0	29.08	12.6	0.66	0.40

TABLE B-II

HIGH TEMPERATURE DEPOSITION TEST RESULTS
525°F LOWER TUBE TEMPERATURE

FORMULATION	NAPTC CODE	DEPOSIT (mg)	VISCOSITY (100°F) @ 48 HRS (cs)	VISCOSITY CHANGE %	TAN @ 48 HRS (mg KOH)	TAN CHANGE (mg KOH)
PE1	L283	0	32.38	18.0	0.78	0.76
		0	32.33	17.8	1.43	1.41
PE2	L214	12	32.80	23.4	1.20	1.18
		12	32.05	17.0	0.75	0.73
PE3	L360	4	30.13	12.2	0.57	0.17
		3	31.15	16.0	1.72	1.32
PE4	L320	5	39.43	35.5	1.61	1.29
		18	39.48	35.7	1.82	1.58
PE5	L340	1	32.29	14.7	0.71	0.68
		1	32.25	14.6	1.11	1.08
PE (Mean)		5.6	33.43	20.5	1.17	1.02
TMP/PE5	L213	4	29.99	16.3	0.73	0.68
		3	30.07	16.6	0.65	0.60
TMP/PE6	L296	18	31.48	18.0	1.38	1.13
		9	31.98	23.9	1.03	0.78
TMP/PE (Mean)		8.5	30.88	18.7	0.95	0.80

TABLE B-III

HIGH TEMPERATURE DEPOSITION TEST RESULTS
550°F LOWER TUBE TEMPERATURE

FORMULATION	NAPTC CODE	DEPOSIT (mg)	VISCOSITY (100°F) @ 48 HRS (cs)	VISCOSITY CHANGE %	TAN @ 48 HRS (mg KOH)	TAN CHANGE (mg KOH)
PE1	L283	40	60.78	121.5	7.05	7.03
		50	53.72	95.8	6.17	6.15
PE2	L364	15	40.09	46.5	1.51	1.35
	L214	20	48.40	76.7	4.77	4.75
PE3	L360	13	33.72	25.6	1.57	1.17
		7	34.88	29.9	1.92	1.52
PE4	L320	12	52.16	81.6	3.35	2.99
		9	47.76	66.3	2.82	2.46
PE5	L340	0	36.08	28.2	1.47	1.44
		7	41.33	46.8	3.73	3.70
PE (Mean)		17.3	44.89	61.9	3.44	3.26
TMP/PE5	L313	28	36.70	42.3	1.78	1.73
		51	62.52	142.5	6.47	6.42
TMP/PE6	L296	100	53.01	105.4	5.82	5.57
		38	43.77	69.6	5.77	5.52
TMP/PE (Mean)		54.2	49.00	90.0	4.96	4.81

TABLE B-IV

ANALYSIS OF RESULTS FROM HIGH TEMPERATURE DEPOSITION TESTS AT 550°F LOWER TUBE TEMPERATURE

STATISTIC	LUBRICANT PROPERTY					
	DEPOSITS		Δ VISCOSITY		Δ TAN	
	PE	TMP/PE	PE	TMP/PE	PE	TMP/PE
Mean	17.3	54.2	61.9	90.0	3.26	4.81
Standard Deviation	15.72	31.92	32.09	43.53	2.10	2.09
F (Calculated)	4.12		1.84		1.01	
F (Table)	5.08		2.81		1.63	
(Probability)	(.05)		(.20)		(.50)	
t (Calculated)	2.97		1.34		1.24	
t (Table)	3.06		1.35		1.35	
(Probability)	(.01)		(.20)		(.20)	

NOTE: All calculations per Compucorp Model 342 Micro-Statistician

APPENDIX C

VAPOR PHASE COKER TEST RESULTS

TABLE C-I

SUMMARY OF PHASE II TESTING RESULTS

FORMULATION	AVERAGE ACID CHAIN LENGTH	VENT TUBE DEPOSITS (mg) AT CONTROL TEMPERATURE OF					BULK OIL LOSS (mg)
		550°F	600°F	650°F	700°F	750°F	
PE-1	6.4	26	100	317	352	295	10.17
PE-2	6.0	16	48	524	227	153	9.72
PE-3	6.4	33	62	153	234	162	7.4
PE-4	6.1	44	-	79	130	77	9.38
PE-5	6.2	17	22	85	160	137	8.22
TMP/PE-5	7.6	14	81	451	500	370	9.1
TMP/PE-6	7.5	21	182	507	432	351	8.0

TABLE C-II

DATA GENERATED BY THE TESTING OF VARIOUS RATIOS OF DIPENTAERYTHRITOL AND TRIMETHYLOL PROPANE ESTERS

650°F Vent Control Temperature

ESTER COMPOSITION % BY WEIGHT		AVERAGE ACID CHAIN LENGTH	DEPOSIT WEIGHT (mg)	BULK OIL LOSS (g)	YIELD % WT.
DPE	TMP				
100	0	6.2	76	29.04	0.26
90	10	6.4	90	27.92	0.32
70	30	6.7	160	27.96	0.57
50	50	7.0	215	31.11	0.69
30	70	7.5	297	28.70	1.04

TABLE C-III

DATA GENERATED BY THE TESTING OF VARIOUS RATIOS OF (MONO) PENTAERYTHRITOL AND TRIMETHYLOL PROPANE ESTERS

650°F Vent Control Temperature

ESTER COMPOSITION % BY WEIGHT		AVERAGE ACID CHAIN LENGTH	DEPOSIT WEIGHT (mg)	BULK OIL LOSS (g)	YIELD % WT.
PE	TMP				
100	0	5.0	186	40.15	0.46
86	14	5.5	194	39.95	0.48
72	28	6.0	191	31.52	0.61
58	42	6.5	211	34.11	0.62
44	56	7.0	283	32.94	0.86
30	70	7.5	366	29.97	1.20

TABLE C-IV

DATA GENERATED BY THE TESTING OF VARIOUS SINGLE ACID ESTERS

650°F Vent Control Temperature

ESTER IDENTIFICATION	DEPOSIT WEIGHT (mg)	BULK OIL LOSS (g)	YIELD % WT.	TEMPERATURE RANGE OF DEPOSIT FORMATIONS (°F) MAX.	TEMPERATURE RANGE OF DEPOSIT FORMATIONS (°F) MIN.	TEMPERATURE AT LOCATION OF HEAVIEST DEPOSITS (°F)
iC_5 DPE	28	30.00	0.09	350	310	-
nC_5 DPE	82	29.10	0.28	415	350	-
nC_7 DPE	157	23.37	0.67	375	<250	-
iC_5 PE	255	35.42	0.72	480	435	440
nC_5 PE	270	33.89	0.80	475	440	450
nC_7 PE	253	29.29	0.86	415	<250	-
nC_9 PE	340	16.46	2.06	400	<250	265
iC_5 TMP	517	71.80	0.72	550	435	450
nC_5 TMP	491	67.13	0.73	540	475	480
nC_7 TMP	591	33.04	1.79	450	340	400
nC_9 TMP	655	22.14	2.90	390	275	285

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