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# THE ANALYSIS AND PROPERTIES OF GERMAN POLYETHYLENE OILS

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# ABSTRACT

Three viscosity grades of the German synthetic "polyethylene" oils have been analysed and studied. They were found to differ from conventional petroleum oils in several respects. They are unique in that they have high V.I.'s and also low pour points and carbon residues. Their superiority as compared to petroleum oils in these respects becomes more apparent for the higher viscosity oils. An examination of some of their pertinent physical and chemical properties led to the conclusion that the polyethylene oils are essentially a mixture of isoolefins. The branch chains are short, and are principally methyl groups.

The least viscous oil with a pour point of -85°F has possibilities as a diesel and jet fuel for low temperature use. Its cetane number is 58. Thus it may also prove useful as a blending agent or diluent for high cetane number fuels with high pour points.

Laboratory oxidation studies and engine tests reveal that the oxidation stability of the polyethylene oils is poor as compared to petroleum oils. The oxidation stability can be improved by the use of antioxidants, certain sulfur type inhibitors being the most effective. Such inhibited oils compare favorably in stability and engine cleanliness with conventional petroleum lubricants.

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## INTRODUCTION

### A. Authorization

1. This investigation was authorized under Bureau of Ships Project Order No. 414/46 dated 7-1-45 concerning the study of petroleum and synthetic lubricant oils and greases.

### B. Statement of the Problem

2. Synthetic lubricating oils are of interest to the Navy as some of them have many desirable properties not found in petroleum oils. The petroleum fractions used in all but the less viscous oils are composed principally of cyclic hydrocarbon nuclei which vary in the number and size of the rings, the degree of condensation of the rings and the degree of unsaturation. A variety of alkyl side chains of different lengths and branching are attached to these nuclei. Hydrocarbons of different structural configurations will differ from petroleum oils in physical and chemical properties. A comparison of the physical and chemical properties of the synthetic oils with petroleum oils and the determination of the differences in structural configuration which account for the differences in properties is of interest and concern to the Navy in the development of new and improved lubricants.

### C. Known Facts Bearing on the Problem

3. One of the more interesting of the German synthetic lubricating oil developments was the polyethylene type oils. As the name indicates, these oils are liquid polymerization products of ethylene. The synthesis and some of the properties of these oils have been described elsewhere (19)(20). Three viscosity grades of the polyethylene oils were obtained by the U. S. Naval Technical Mission in Europe and sent to this laboratory for examination. The oils coded as SS (Schmierstoff)-903 and SS-906 were identified as aircraft engine oils. The oil coded as V-120 was identified as a lubricant for rocket and jet propelled aircraft. According to the technical mission reports (19)(20), the polyethylene oils were blended with other oils, either petroleum or synthetic for use as lubricants. It was inferred that in general the blending with other oils was practiced to extend the supply and reduce the number of viscosity grades produced and not because of the inferiority of the straight polyethylene oils as lubricants. Copolymerization with petroleum lubricating oil fractions was also employed as the product resembled the pure polyethylene oil more closely than the petroleum oil blends.

## DISCUSSION OF RESULTS

### A. Properties of Interest as Lubricants

4. This discussion is concerned with the results of a study by this laboratory of many of the physical and chemical properties and characteristics of the straight polyethylene oils. Some of the properties of interest as lubricants are shown in Table I. The German specifications for the various grades are also shown there. A.S.T.M.(2) test methods were used in all cases where an applicable procedure was given. The A.S.T.M. color numbers of the polyethylene oils are not radically different from those of U.S. commercial petroleum oils of similar viscosity grades. However, it is unusual to find the less viscous SS-903 oil darker than the SS-906. The Germans did not have a color requirement in their specification, only the general requirement that the oil be clear and free of undissolved material. It is not known which of these oils is the more typical, as regards color, of the German production. In general, it has been observed at this laboratory that German petroleum oils were not refined to as light a color as comparable U.S. petroleum oils. Like petroleum oils, the polyethylene oils may be decolorized by adsorbents such as Fuller's Earth.

5. The Cleveland open cup flash and fire points of the polyethylene oils are shown in the table. The German standard instrument for this determination is the Marcusson open cup and the correlation between these two instruments is not known. The C.O.C. flash point of the SS-903 oil is on the border line of the German specification requirement, and the other two oils exceed the requirement. The polyethylene oils have much lower flash and fire points than conventional petroleum oils of the same viscosities. This may in part be due to the presence of low molecular weight polymerization products of ethylene, but the differences observed are so great that they are attributed to differences in structural configurations. The spontaneous ignition temperatures using the apparatus described by Sortman, Beatty and Herron (17) were not greatly different from petroleum oils of comparable viscosity.

6. The viscosities of these oils at various temperatures are given in both centistokes and Saybolt universal seconds. The German viscosity limits in Engler degrees were converted to centistokes by the tables and formulae given by Barnard (3). The V-120 oil with a viscosity of 10.2 cs. at 20°C (68°F) is well above the minimum viscosity required, 8.6 cs. However, at -60°C (-76°F) the viscosity

obtained by the extrapolation of the viscosity temperature graph from -40°F to -76°F was 6000 cs. as compared to the requirement of 2500 cs. It is realized that such extrapolations are frequently inaccurate, but in general the extrapolated value is lower than the experimental value. Thus, it is concluded that the V-120 oil greatly exceeds the German specification requirement at -60°C (-76°F). The Kinematic Viscosity Index or K.V.I. of this oil is 96 which is not unusual for certain petroleum fractions of similar viscosity. An oil conforming to the German specification, of a minimum of 8.6 at 68°F and a maximum of 2508 cs. at -76°F would be exceptional.

7. The SS-903 and SS-906 oils are much more viscous, the former falling in SAE 50 viscosity grade and the latter in SAE 140 grade. Both oils are on the border line of the German viscosity requirements at 122°F and 212°F. Oil SS-903 with a K.V.I. of 110 is below the specification requirement of 115. The SS-906 oil with a K.V.I. of 109 exceeds the specification requirement of 107. Compared to petroleum oils the observed K.V.I.'s of these oils are excellent. This is particularly true of the more viscous grade as the V.I. scale is less favorable to oils of the higher viscosities. For example, V.I.'s of 100 and above are not uncommon for petroleum oils up to the SAE 40 viscosity grade, whereas for the more viscous oils, V.I.s above 95 are unusual. The kinematic viscosity vs. temperature graphs on ASTM Viscosity-Temperature Chart D 341-43 are essentially straight lines for all of the polyethylene oils over the temperature range investigated.

8. The V-120 oil has a pour point of -85°F. This is unusually low for petroleum fractions of similar viscosity, most aviation gasolines have freezing points around -75°F. The SS-903 oil has a pour point of -20°F. For comparison, the grade 1100 oil (93-103 S.S.U. at 210°F) of Army-Navy Aeronautical Specification AN-O-8 for "Oil; Lubricating Aircraft Engine" has a pour point requirement of +10°F (max.). The SS-906 oil has a pour point of -10°F which is exceptional for an oil of this viscosity. Though these oils have exceptionally low pour points as compared to similar petroleum products, they all fail the German specification requirements. These oils also differ from petrolem oils in that their Conradson carbon residues are very low. The SS-903 oil has a slightly higher value (0.18%) than the SS-906 (0.14%). For comparison, the grade 1100 oil of specification AN-O-8, mentioned above, allows carbon residues up to 1.2%.

9. The polyethylene oils like well refined petroleum oils have low neutralization, saponification and precipitation numbers. They do not tarnish copper after 3 hours at 212°F and have little or no inorganic constituents present. It is probable that the trace of ash observed in the aircraft engine oils was due to the presence of rust in the containers. The polyethylene oils have sulfur contents of less than 0.05% which is much lower than that of conventional petroleum lubricating oils.

## B. Investigation of Molecular Formula and Structure

10. The average molecular weights of the polyethylene oils were determined ebullioscopicly using the apparatus described by Washburn and Read (22). Thiophene-free benzene dried over sodium was used as the solvent. The molal boiling point elevation of the benzene was determined experimentally using carefully purified samples of hexadecane and naphthalene and found to be 2.542 ± 0.24%. The molecular weights shown in Table I are the averages of triplicate determinations. The molecular weights of the polyethylene oils are somewhat higher than those of petroleum oil fractions (8) (12) of equal viscosities. Micro-determinations of the carbon and hydrogen contents were made in duplicate and the values reported are the mean. The hydrogen content and the hydrogen to carbon ratios are higher than those of petroleum oils. The molecular formulae were calculated after adjusting the sum of the carbon and hydrogen contents to 100%.

11. The empirical or general formulae of the polyethylene oils show that the hydrogen deficiency increases with increasing molecular weight. The hydrogen deficiency could be due to the presence of unsaturated linkages or cycloparaffin groups which (10) (11) (14) (23) have been shown to be present in the polymerization products of ethylene. The decolorization of bromine by the polyethylene oils shows the presence of unsaturated bonds. The number of double bonds per molecule was calculated on the assumption that the polyethylene oils contained no cyclic groups. Evidence for the absence of such groups will be discussed later. As the molecular weights of the polyethylene oils differ greatly in magnitude, the degree of unsaturation would be better expressed on a comparable weight basis. Expressed as the number of double bonds per 100 molecular weight, the ratios are 0.238, 0.270 and 0.234 for the V-120, SS-903 and SS-906 oils respectively. Therefore, the degree of unsaturation of the polyethylene oils is approximately the same, the SS-903 oil being slightly greater than the other two oils.

12. The specific gravities of the polyethylene oils are much lower than those of petroleum fractions (8) (12) of comparable viscosity and molecular weight. The Pennsylvania type or "paraffin base" oils have specific gravities more nearly approaching those of the polyethylene oils than any of the petroleum oil types. The Pennsylvania type oils are composed of cyclo-paraffin or naphthene nuclei with alkyl side chains. Petroleum oils containing aromatic nuclei have much higher specific gravities. The properties of synthetic high molecular weight hydrocarbons (5) (13)(15) (16) confirm the generalizations that there is a progressive increase in specific gravities of the paraffin, cycloparaffin and aromatic hydrocarbons. The specific gravity of an olefin is greater than that of a paraffin with the same structural configuration, but insufficient data is available to make generalizations as to how they compare with the cycloparaffins. The specific gravities of the polyethylene oils are higher than those calculated for isoparaffins of similar molecular weight by Francis" method (9). The presence of olefins in the polyethylene oils would account for at least the greater part of the differences observed. The aniline points of the polyethylene oils are high as compared to petroleum fractions. This is confirmatory evidence of the absence of aromatic constituents and conjugated olefins.

13. The refractive indices and related optical properties are well known to be useful in helping to establish the structure of hydrocarbons and petroleum oils. The refractive indices of the polyethylene oils were determined with light of the following wave lengths; hydrogen C (4861°A), mercury green (5461°A) sodium D (5893A° and hydrogen F (6563°A). A Bausch and Lomb precision Abbe refractometer was used in making these determinations. The SS-903 and SS-906 oils were so highly colored that a precise value could not be obtained for light of 4861°A. The values reported at this wave length were obtained by extrapolating the straight line graph of n vs $1/\lambda^2$(Cauchy formula). The refractive indices for sodium D light ($N_D^{20^\circ C}$) are lower than those of petroleum oils (8). A comparison with the reported results for synthetic hydrocarbons (5) (13) (15) (16) reveal that the polyethylene oils have refractive indices lower than those of substituted cycloparaffin and aromatic compounds but higher than the isoparaffins. Olefins have higher refractive indices than the corresponding paraffins due to the exaltation caused by the double bond. The number and nature of the branch chain has a variable and less predictable effect on the refractive index. Thus by comparison it appears that these synthetic oils are probably branched chain olefins.

14. The specific dispersion, the difference in the refractive indices for two wave lengths of light divided by the density, has been especially useful in characterizing the structure of hydrocarbons. Dispersions are most commonly given for the interval between the hydrogen F and C lines. Ward and Kurtz (21) have prepared one of the more complete tabulations of the dispersions of various hydrocarbon types. The paraffins and cycloparaffins have specific dispersions of approximately $99 \times 10^{-4}$. Olefins, diolefins and aromatics have higher specific dispersions depending on the amount of unsaturation, configuration and molecular weight of the molecule. The specific dispersions of mono-olefins tend to approach that of paraffins at high molecular weights. As the polyethylene oils have specific dispersions of 100 to $102 \times 10^{-4}$, it is unlikely that they contain conjugated olefins or aromatic constituents.

15. The Lorenz and Lorentz specific refraction $\left(r = \frac{n^2-1}{n^2+2} \cdot \frac{1}{d}\right)$ and the molar refraction (defined as r x mol. wt.) are also helpful in characterizing the structure and composition of compounds. For saturated hydrocarbons, it has been established that the experimentally determined molecular refractions are equal to the sum of the atomic refractions. For unsaturated and aromatic hydrocarbons the calculated values are lower than the observed values. Thus the molecular refraction is not a simple additive function but is also influenced by the structural configuration of the molecule. Eisenlohr (6) (7) values for the aromatic refractions are most commonly used and are as follows $n_D^{20°C}$

$C = 2.418$
$H = 1.100$
$C = C = 1.733$ exaltation due to an isolated double bond.

It is seen from Table I that the experimentally determined values of the molecular refraction agree quite well with the values calculated from the molecular formulae. The differences observed are well within the accuracy of the molecular weight and ultimate analysis determinations. Therefore, the average molecular formulae assigned to the various polyethylene oils are considered substantially correct. The conclusions previously drawn, that there are no conjugated olefinic structures or aromatic constituents present, is further confirmed.

16. The absorption spectra of the polyethylene oils in the ultra-violet and infrared regions were determined by Messrs. J. J. O'Neill and D. C. Smith (24) of this laboratory. These spectra confirm the absence of aromatic components.

The infrared spectra of the oils show that they are chain-like hydrocarbons having an occasional double bond not at the end of the molecule and not adjacent to the branching centers. All these oils have approximately the same number of double bonds per unit length of chain. These spectra also revealed that the polyethylene oils contained a few branch chains, mostly methyl groups, some attached near the ends of the chain and others attached elsewhere. The higher molecular weight oils appear to have fewer methyl branches, the SS-906 oil having no branches at the ends of the chain. The spectra of these polyethylene oils differ most in that SS-903 shows strong carbonyl oxygen absorption, the V-120 oil much less and the SS-906 oil exhibits no definite carbonyl absorption.

17. The V-120 oil was distilled under a pressure of 1 to 2 mm of mercury through a 5/8 inch diameter column packed to a depth of 10 inches with glass helices. Some of the properties of interest of the various fractions are given in Table II. The data reveals that the oil is a mixture of molecules of varying molecular weights as reflected by the increases in boiling points, viscosity and aniline points. Even at pressures of 1 to 2 mm., cracking was apparent before the temperature reached 250°F. The distillation had to be stopped when the temperature reached 284°F, as it was impossible to maintain a pressure as low as 2 mm. because of cracking. The specific dispersions of the distillation cuts are higher than that of the original oil. This is additional evidence of cracking, as the specific dispersion increases with the degree of unsaturation. The SS-903 oil was distilled in the same apparatus but under lower initial pressures, 0.2 to 0.4 mm. of mercury. As in the distillation of the V-120 oil, the pressure increased due to cracking and when the temperature reached 280°F., the distillation had to be stopped as the decomposition became excessive. The fractions collected showed a progressive increase in viscosity and aniline points similar to those of the V-120 oil. No attempt was made to distill the SS-906 fraction.

18. The results of this phase of the investigation on the polyethylene oils leads to the conclusion that they differ considerably from petroleum oils in structure and in some properties. It is concluded that they are essentially a mixture of isoolefins. The degree of unsaturation is approximately the same for the three oils received. Expressed as the number of double bonds per 100 molecular weight, the ratio is approximately 0.25. The infrared absorption spectra reveal that the branch chains are essentially methyl groups. The amount of branching is less in the higher molecular weight oils which is reflected by their higher V.I.s. The molecular refractions calculated from the atomic refactions and the average molecular formulae agree quite well with the experimentally determined values.

## C. Properties of Interest as Fuels for Diesel and Aircraft Jet Engines

19. Low pour point fuels for diesel and aircraft jet engines are needed for military applications. The straight chain or normal paraffin hydrocarbons have been shown to have better ignition characteristics as diesel fuels than the branched chain or cyclic hydrocarbons. However, the straight chain compounds have such high pour points that their use as diesel fuels even in temperate climates is not practical. Therefore, some compromise in ignition quality must be made to obtain the low pour points needed. Low point fuels with ignition qualities superior to those of petroleum oils are desired. The possibility of the V-120 polyethylene oil as a diesel fuel was first suggested by its high aniline point and low pour point.

20. Many formulae and equations have been devised attempting to correlate the ignition characteristics of diesel fuels with physical and chemical properties. One of the most commonly employed is the Diesel Index Number or D.I. of Becker and Fischer (4).

$$D.I. = \frac{A.P.I.\ Gravity\ X\ Aniline\ Pt.\ {}^{O}F}{100}$$

The D.I. of the V-120 was found to be 84. Such a rating is unusual for petroleum fuels. No definite correlation has been found between the D.I. and the ignition qualities as determined by the motor method, but the two methods agree very well for conventional "undoped" fuels. It was not known how the two methods would correlate for a synthetic fuel that differed from petroleum fuels in structure. However, as the V-120 oil was in the viscosity range of diesel fuels, a direct comparison of its properties with current specification requirements was made. Table III shows that the V-120 oil conforms to all the requirements of Grade A fuel of U.S.Army specification No. 2-102C and the Navy Department Bureau of Ships specification 7-0-2 (INT). The V-120 oil is decidedly superior to specification oils as regards flash, pour points and sulfur content.

21. The "cetane number" was determined by the U.S. Naval Engineering Experiment Station and found to be 58 which is a considerably lower rating than obtained by the D.I. method. Therefore, the D.I. rating is not a reliabe method of characterizing the ignition qualities of the synthetic polyethylene oils as it gives them too high a rating. According to the cetane rating, this oil has better ignition characteristics than the majority of petroleum fuels and should make a good low pour-point diesel fuel. It may also prove useful as a blending agent to depress the pour point of the high cetane number fuels such as those made by the Ficher Tropsch process.

22. The heats of combustion are of interest for oils proposed as fuels. These were calculated at both constant volume and pressure for the V-120 oil from its density, by the graphical interpolation of the values given by the Bureau of Standards (18). As the heats of combustion of hydrocarbons increase with density or carbon content, the polyethylene oils have lower heats of combustion than do similar viscosity petroleum products.

## D. Laboratory Thermal and Oxidation Stability Studies

23. Some information as to the thermal and oxidation stability of any fluid proposed as a lubricant is necessary before its possible usefulness and range of application can be predicted. The polyethylene oils were oxidized in the all-glass system elsewhere described by this laboratory (1) at 100°C with air. A 25 gram sample was used and the air flow rate was 20 ml/min. The test was of 168 hours duration. Other tests were made when the oil was oxidized in contact with metals. The metal specimens used were of electrolytic copper, 24 ST duralumin and SAE 1020 cold rolled steel which were polished and degreased. They were $1\text{-}\frac{1}{2}$"x$\frac{1}{2}$"x1/16" and had a surface area of 1.75 sq. in. or 11.12 sq. cm. When all three metals were used in the oxidation test they were arranged in the form of a triangle with the long edges in contact with the other specimens.

24. The viscosities and neutralization numbers were determined before and after each test and the changes in these properties were used as criteria of the stability of the oil. The effluent gases from the oxidation cell assembly were bubbled into a known volume of standard alkali and back-titrated at intervals to determine the amount of volatile acidic products. The number of mg. of KOH required to neutralize the volatile acidic products formed per gram of oil charge was calculated and referred to as the volatile acid neutralization number.

25. The results of the oxidation tests at 100°C, summarized in Table IV, reveal that the SS-903 oil is the most stable to oxidation in the all-glass system. The V-120 and SS-906 oils showed large increases in neutralization numbers and viscosities. The V-120 oil also had a high evaporation loss and volatile acid neutralization number. The presence of cold rolled steel in the system did not materially effect the oxidation reactions of the SS-oils. The V-120 oil in the presence of cold rolledsteel showed a smaller neutralization number increase, viscosity change and evaporation loss. However the volatile acid neutralization number was much higher. As the SS-903 oil was quite stable to oxidation at 100°C in a glass system and also in the presence of cold

rolled steel, another test was made including copper and duralumin in the system. Copper is known to be a powerful oxidation accelerator for petroleums, hydrocarbons and vegetable oils. The aluminum alloys of the duralumin type are much weaker accelerators. When all three of the metals were present, the SS-903 oil was evidently more highly oxidized.

26. It is well known that certain materials, even when present in small concentrations, act as inhibitors retarding the rate and possibly the course of the oxidation reaction. Phenolic type compounds have been found to be effective antioxidants particularly at the lower temperatures. A typical phenolic antioxidant, 4-tert butyl-2-phenylphenol, was used in the polyethylene oils in 0.2% weight concentrations. In the all-glass system this concentration was able to inhibit the oxidation of the V-120 and SS-906 oils until they were approximately as stable as the uninhibited SS-903 oil. The inhibited V-120 oil had a much smaller evaporation loss and volatile acid neutralization number than the straight oil. This indicates that the evaporation loss of the uninhibited oil is due to the scission of the oil molecules by oxidation and also accounts for the large amount of volatile acidic products evolved. When the inhibited oils were oxidized in the presence of metals, they showed improved resistance to oxidation although they increased in viscosity and neutralization numbers. The 4-tert-butyl-2-phenylphenol was the most effective as an antioxidant in the V-120 oil as shown by the smaller increases in neutralization numbers and viscosity. The viscosity changes observed in this oil werealso influenced by the evaporation of the more volatile and less viscous components.

27. As a temperature of 100°C is rather mild for the evaluation of crankcase lubricants, the temperature was raised to 130°C for additional tests. All tests at this temperature were made in the presence of metals as they are always present under service conditions. As it was desired to make small scale engine tests on the polyethylene oils, the SS-903 and V-120 oils were blended to SAE 30 viscosity requirements. The blend contained 76% by weight of the SS-903 oil. As would be expected the uninhibited oils are more highly oxidized at 130°C than at 100°C. Typical amine, phenolic, phosphite and sulfur-type inhibitors were investigated at this temperature. The data shown in Table V reveals that certain sulfur type antioxidants were the most effective of the inhibitors investigated. The polyethylene oils inhibited by phenothiazine and thio-$\beta$-naphthol compare favorably in stability with the better petroleum oils.

## E. Engine Tests

28. The uninhibited blend of the SS-903 and V-120 oils and the blend with 1% of hexadecyl thioether as an antioxidant were evaluated in a General Motors 1-71 diesel engine under the requirements of specification 14-0-13a, namely 15 B.H.P.; 1200 R.P.M.; 175°F coolant temperature and 230°F crankcase oil temperature. The test was of 300 hours duration and was carried out by the U.S. Naval Engineering Experiment Station. When the engine was lubricated with the uninhibited oil the test had to be discontinued after 190 hours as it was impossible to maintain the specified temperatures. This was due to the large increase in viscosity of the oil, which could be predicted from the laboratory oxidation tests. The oil inhibited with hexadecylthioether caused no apparent difficulties in engine operation. The engine ratings after use of these blends as compared to specification requirements are shown in Table VI. The data shown there reveals that when the engine was lubricated with the inhibited blend it exceeded the "Engine Cleanliness" requirements on two counts, "Ring Groove Deposits" and "Oil Ring Holes". The engine wear was well within the specification limits. The oil after the 300 hour test had not increased excessively in neutralization number, precipitation naphtha, or chloroform insolubles. The viscosity increase was rather high but this was caused chiefly by the evaporation of the lighter V-120 component. It would seem quite probable that the addition of an effective detergent would reduce the amount of engine deposits. It is unfortunate that the laboratory oxidation studies were not completed when the engine tests were made so that one of the more effective antioxidants, thio-B- naphthol or phenothiazine could have been used.

29. The laboratory oxidation studies and engine test results show that the polyethylene oils are not sufficiently stable to oxidation to be used as lubricants. However, it is possible to improve their resistance to oxidation by the use of antioxidants. The sulfur containing antioxidants were the most effective of those studied, and the oils inhibited with them compared favorably with petroleum oils in stability. The cleanliness of the G.M. 1-71 diesel engine after 300 hours operation when lubricated with polyethylene oil also compared favorably with petroleum oil lubricants. It seems probable that detergents could be used as effectively in polyethylene as in petroleum oils.

## CONCLUSIONS AND RECOMMENDATIONS

30. The German polyethylene oils are essentially iso-olefins, having a long chain-like structure and an occasional double bond not at the end of the molecule nor adjacent to the beanching centers. The branched chains are short, principally methyl groups. The higher molecular weight oils SS-903 and SS-906 appear to have fewer branched chains. This is reflected by their better viscosity-temperature characteristics as compared to the V-120 oil.

31. The polyethylene oils are superior to petroleum oils in several respects. They have excellent V.I.s and are unique in that they also have very low pour points and carbon residues. These desirable characteristics are attributed to differences in their structural configurations as compared to petroleum oils. These oils contain little if any sulfur or other inorganic constituents and are non-corrosive to copper.

32. The less viscous polyethylene oil with a pour point of -85°F has possibilities as a fuel for diesel and air-craft jet engines. This oil has a cetane rating of 58 which is exceptional for such a low pour point fuel.

33. Laboratory oxidation studies and engine tests reveal that the oxidation stability of the polyethylene oils is poor as compared to petroleum oils. However, the oxidation stability can be greatly improved by the use of antioxidants, certain sulfur type inhibitors being the most effective. These inhibited oils compare favorably in stability and engine cleanliness with conventional petroleum oils.

34. It is recommended that the Navy continue its investigation of these synthetic oils as lubricants for applications requiring oils of low pour points and high V.I. Viscosity grades intermediate to those studied should be obtained for investigation.

35. The possibilities of these oils as synthetic fuels should be further investigated. In particular their use as blending agents or diluents for high pour point and high cetane number fuels should be studied.

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TABLE I

Properties of Polyethylene Oils

| | V-120 | | SS-903 | | SS-906 | |
|---|---|---|---|---|---|---|
| | Experimental | German Spec. | Experimental | German Spec. | Experimental | German Spec. |
| A.S.T.M. Color Number | 2 | (1) | 8 | (1) | 6 | (1) |
| Flash Point C.D.C., °F | 245 | 248(min)(2) | 385 | 392(min)(2) | 450 | 437(min)(2) |
| Fire Point C.O.C., °F | 270 | - | 440 | - | 535 | - |
| Spontaneous Ignition Temp. °F | 492 | | 770 | | 804 | |
| Viscosity, centistokes at 212°F | 1.85(3) | | 19.4(3) | 21(max) | 42.(3) | 42(min) |
| 210°F | 1.87 | | 20.1 | | 42.8 | |
| 130°F | 4.02 | | 94.4 | | 253. | |
| 122°F | 4.4(3) | | 116.(3) | 106-114 | 325.(3) | 334-350 |
| 100°F | 6.04 | | 219. | | 658. | |
| 77°F | 8.7(3) | | 469. | | 1600. | |
| 68°F | 10.2(3) | 8.6(min) | 660.(3) | | 2400.(3) | |
| 32°F | 32.9 | | 3480 | | 15600. | |
| 0°F | 67.4 | | 25000 | | - | |
| -40°F | 441. | | - | | - | |
| -76°F | 6000.(3) | 2508(max) | - | | - | |
| Viscosity, S.S.U. at 210°F | $<$ 32. | | 98.2 | | 198.3 | |
| 130°F | 39.2 | | 437. | | 1170. | |
| 100°F | 45.6 | | 1012. | | 3040. | |
| 77°F | 54.3 | | 2160. | | 7380. | |
| 32°F | 114. | | 16000. | | 71800. | |
| Kinematic Viscosity Index | 96 | | 110 | | 109 | |
| Pour Point, °F | -85 | -94(max) | -20 | -31(max) | -10 | -13(max) |
| Conradson Carbon Residue, % | trace | | 0.18 | 0.2(max) | 0.14 | 0.2(max) |
| Neutralization Number | 0.05 | 0.06(max) | 0.05 | 0.06(max) | 0.03 | 0.06(max) |
| Saponification Number | $<$ 0.5 | | $<$0.5 | | $<$0.5 | 0.3(max) |
| Precipitation Number | nil | | nil | | nil | |
| Copper Corrosion: 3 hrs. at 212°F | nil | | nil | | nil | |
| 24 hrs. at 212°F | v.sl.tar. | | v.sl.tar. | | v.sl.tar. | |
| Ash, % | nil | nil | trace | nil | trace | nil |
| Sulfur, % | $<$0.05 | | $<$0.05 | | $<$0.05 | |
| Specific Gravity 20°/4°C | 0.815 | 0.816(max) | 0.851 | 0.860(max) | 0.852 | 0.862(max) |
| 60°/60°F | 0.819 | | 0.855 | | 0.856 | |
| A.P.I. Gravity | 41.3 | | 34.0 | | 33.8 | |
| Aniline Point, °F | 204 | | 282 | | 306 | |
| Average Molecular Weight | 252±1% | | 649±1% | | 854±2% | |
| Carbon Content, % | 85.52 | | 85.92 | | 85.86 | |
| Hydrogen Content, % | 14.69 | | 14.20 | | 14.18 | |
| Formula | $C_{17.9}H_{36.6}$ | | $C_{46.4}H_{91.3}$ | | $C_{61.0}H_{120.0}$ | |
| Empirical Formula | $C_nH_{2n+0.6}$ | | $C_nH_{2n-1.5}$ | | $C_nH_{2n-2.0}$ | |
| Double Bonds per Molecule | 0.65 | | 1.75 | | 2.00 | |
| Refractive Index $n_F^{20^\circ C}$(4861°A) | 1.4586 | | 1.4792(4) | | 1.4800(4) | |
| $n_{Hg\ green}^{20^\circ C}$(5461°A) | 1.4548 | | 1.4752 | | 1.4762 | |
| $n_D^{20^\circ C}$(5893°A) | 1.4529 | | 1.4730 | | 1.4739 | |
| $n_C^{20^\circ C}$(6563°A) | 1.4504 | | 1.4705 | | 1.4715 | |
| Dispersion $(n_F-n_C) \times 10^4$ | 82 | | 87 | | 85 | |
| Specific Dispersion $\left(\frac{n_F-n_C}{d}\right) \times 10^4$ | 101 | | 102 | | 100 | |
| Specific Refraction | 0.332 | | 0.330 | | 0.330 | |
| Molar Refraction (experimental) | 83.5 | | 214 | | 282 | |
| Molar Refraction (calculated) | 84.7 | | 216 | | 283 | |

Legend

(1) The oil shall be clear, free of undissolved water, mineral acids and solid foreign material.

(2) Marcusson Open Cup.

(3) Interpolated or extrapolated from A.S.T.M. Viscosity-Temperature Chart.

(4) Extrapolated by use of Cauchy formula.

## Table II

### Vacuum Distillation of Polyethylene Oil V-120

| Fraction | Dist. Range°F | Pressure mm. | Wgt. % | Visc. cs. at 100°F | Sp. Dispersion x $10^4$ * | Aniling Point °F |
|---|---|---|---|---|---|---|
| 1 | 122-221 | 1.2 | 2.1 | 1.90 | 106 | 167.7 |
| 2 | 221-234 | 1.2 | 8.1 | 2.45 | 106 | 177.1 |
| 3 | 234-236 | 1.2 | 8.7 | 2.92 | 109 | 182.7 |
| 4 | 236-242 | 1.2 | 9.2 | 3.40 | 106 | 187.0 |
| 5(a) | 176-246 | 1.3 | 5.2 | 3.92 | 109 | 190.8 |
| 6(b) | 246-217 | 1.3 | 5.1 | 4.15 | 109 | 192.2 |
| 7 | 217-232 | 1.3 | 4.5 | 4.17 | 108 | 191.3 |
| 8(c) | 244-266 | 1.8 | 5.3 | 6.38 | 109 | 204.3 |
| 9 | 266-280 | 1.8 | 9.4 | 6.71 | 109 | 205.2 |
| 10 | 280-284 | 1.8 | 1.9 | 7.14 | 109 | 205.7 |
| Residue | - | - | 40.5 | 22.8 | 103 | 233.8 |
| V-120 Oil | - | - | - | 6.04 | 101 | 204.2 |

(a) Distillation stopped and started again the next day.
(b) Cracking occurred and temperature dropped.
(c) Pressure increased to 1.8 mm. due to cracking.

* $\frac{n_f-n_c}{d}$

### Table III

### Properties of Polyethylene Oil, V-120 of Interest as a Diesel Fuel

| | Army Spec. No.2-102C Grade A | Bureau of Ships Spec. 7-0-2(INT) | German Polyethylene Oil V-120 |
|---|---|---|---|
| Flash Point, P.M.C.C., °F | 140 | 150 | 222 |
| A.S.T.M. Color Number | 5 | 5 | 2 |
| Pour Point, °F | (a) | 0 | -85 |
| Viscosity, cs. at 100°F | 2.5 to 6.0 | - | 6.04 |
| Viscosity, S.S.U.at 100°F | - | 35 to 45 | 45.6 |
| Water and Sediment, % | 0.05 | 0.05 | nil |
| Total Sulfur, % | 1.25 | 1.00 | < 0.05 |
| Carbon Residue(10% Bottoms) % | 0.15 | 0.20 | 0.13 |
| Ash, % | - | 0.01 | nil |
| Copper Corrosion: 3 hrs. at 212°F | pass | pass | nil |
| Distillation | | | |
| First Drop | - | - | 443 |
| 10% distilled, °F | - | - | 502 |
| 30% " " | - | - | 533 |
| 50% " " | - | - | 563 |
| 70% " " | - | - | 603 |
| 90% " " | 675 | 675 | 670 |
| End Point | 725 | - | 691 (b) |
| Diesel Index Number | - | 53 | 84 |
| Cetane Number | 40 | 50 | 58 |
| Heat of Combustion | | | |
| Constant Volume | | | |
| Btu/lb. | | | 19,790 |
| Btu/gal. | | | 135,100 |
| Constant Pressure | | | |
| Btu/lb. | | | 18,540 |
| Btu/gal. | | | 126.600 |

(a) Shall be 10% below the lowest atmospheric temperature expected.

(b) 95% distilled before cracking.

Table IV

Dynamic Oxidation Tests at 100°C on Polyethylene Oils

| t | Conc. of Antiox.% | Metals Present | Neutralization No. Before | Neutralization No. After | Visc. cs. at 100°F Before | Visc. cs. at 100°F After | Volatile Acid Neut. Number | Weight Loss, 0/0 |
|---|---|---|---|---|---|---|---|---|
|  |  | - | 0.03 | 60.5 | 6.09 | 48.3 | 19.87 | 14.0 |
|  |  | Fe | 0.03 | 49.9 | 6.09 | 23.5 | 31.32 | 8.0 |
| -2-phonylphenol | 0.2 |  | 0.08 | 0.44 | 6.09 | 6.50 | 4.11 | 2.6 |
| -2-phenylphenol | 0.2 | Fe.Cu.Du | 0.08 | 0.81 | 6.09 | 6.75 | 4.50 | 3.8 |
|  | - | - | 0.07 | 0.13 | 219. | 229. | 2.55 | 0.3 |
|  | - | Fe | 0.07 | 0.14 | 219. | 230. | 2.51 | 0 |
|  | - | Fe.Cu.Du | 0.08 | 9.6 | 219. | 424 | 8.56 | -2.0 |
| -2-phenylphenol | 0.2 | Fe.Cu.Du | 0.08 | 1.77 | 219. | 271. | 6.13 | -0.6 |
|  | - | - | 0.06 | 6.1 | 658. | 1360. | 4.90 | 1.6 |
|  | - | Fe | 0.06 | 6.1 | 658. | 1270. | 2.92 | -1.6 |
| -2-phenylphenol | 0.2 | - | 0.06 | 0.18 | 654. | 728 | 5.34 | 0.0 |
| -2-phenylphenol | 0.2 | Fe.Cu.Du | 0.06 | 1.75 | 654. | 858 | 5.93 | -0.8 |