

ATTACHMENT VIII

The Scientific Basis for Lubricating Oil Synthesis

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May 14, 1943

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I. G. Leuna Report of May 14, 1943 by Dr. H. Zorn.

Indeed, chemistry resembles Proteus who is capable of appearing in many guises. Sometimes she (chemistry) appears as a goddess, sometimes as a fickle woman. Still we are glad to have her, for underneath her taunting and deceptive pranks she conceals eternal truths.

These words were spoken by the great experimenter Ludwig Claissen to his friend Anwers on New Year's 1927. In the same year I was introduced to the field of lubricants and very soon learned the "taunting and deceptive pranks" which these materials played upon chemists at that time. In the following tables and graphs I will demonstrate the rules which are concealed in these taunting pranks and explain how we succeeded in developing a genuine commercial synthesis.

The earliest experiments on the synthetic preparation of lubricating oils date back to the time of the first World War. At that time, Dr. Schneider attempted to prepare lubricating oils by polymerizing unsaturated components from the Brown Coal (gas) generators. We engaged in this work again in 1926 by the method of passing gaseous olefins into tar oils and "Hydrier" oils in the presence of aluminum chloride. This process was carried out during 1930-1931 in a large-plant-scale trial here in Leuna. However, no motor oils of great value were thus obtained, but only machine oils. Nevertheless, these experiments were the beginning of an exhaustive study of means for polymerizing chemically pure olefins of well-known constitution.

Some results of this investigation are shown in Table 1. It is clear that only straight-chain olefins with a terminal double bond produce polymers in good yield which are characterized by good viscosity-temperature behavior. Yields and V.I. are both poor when the double bond is located in the middle of the molecule or when a hydrogen atom of the terminal double bond is substituted by an alkyl group. It is noteworthy that dimethyloctylene produces a polymer of very high viscosity in good yield. The results of this fundamental investigation were developed technically into the process for the polymerization of cracked wax.

Straight-chain olefins bearing a terminal double bond are formed in the gas-phase cracking of wax. The polymerization of these olefins is shown in Figure 2. In order to determine whether this mechanism is correct, we have attempted to synthesize hydrocarbons of the same type as those represented in the figure above. The synthesis shown in Figure 3 (illegible), was developed and carried out by Dr. Metzger and Dr. Nienburg. We started with octaldehyde which was converted into hexyl-heptyl-acrolein (by the aldol condensation), and this was reduced to the corresponding alcohol (with a nickel-kieselgur catalyst). The product was converted into the corresponding 2-hexyl-1-iododecane (by means of iodine and red phosphorus) which was treated with the sodium salt of the ethyl ester of hexylmalonic acid. The ester thus obtained was saponified, decarboxylated, and the resulting acid again reduced to alcohol. The alcohol thus obtained was again converted to the iodide

(with phosphorus and iodine) which was either reduced to the hydrocarbon or again treated with the sodium salt of the ethyl ester of hexylmalonic acid so as to give the next higher homolog. In this way, which was troublesome but very exact, the hydrocarbons shown in Table 4 (illegible) were prepared.

It is evident in the homologous series 1 to 5 that the viscosity increases and the viscosity-temperature behavior continually improves with increasing molecular weight. The same holds true for the homologs 6, 7, and 8. These hydrocarbons were obtained from the iodides by means of the Wurtz synthesis. In this way, we succeeded in preparing a hydrocarbon  $C_{64}H_{130}$  with a molecular weight of 899. This is a molecular weight which lies in the middle of the steam-cylinder oil range (i.e., high-molecular mineral oils). Thus the exact synthesis of a high-molecular lubricating-oil hydrocarbon was accomplished for the first time. The low melting points of all these materials are noteworthy; specifically, the last mentioned hydrocarbon has a melting point of  $-39^{\circ}C$ .

In Table 5 (illegible) is shown how the viscosity-temperature behavior varies with intramolecular carbon-chain branching for molecules of the same weight. It is evident that the viscosity-temperature behavior improves with decrease in the number of side chains.

Table 6 (missing) likewise shows the influence of the type of chain branching on the viscosity-temperature behavior for molecules of the same size. The greater the degree of branching, the poorer is the viscosity-temperature behavior and the higher the viscosity. The closer that the form of the molecules approaches a sphere (i.e., compact form) the more unfavorable is the influence of temperature on viscosity.

Table 7 shows similar phenomena for  $C_{16}$  and  $C_{24}$  hydrocarbons. Short side chains or branched side chains are very unfavorable as shown by hydrocarbons 9 and 10. The influence of short side chains on melting point is very interesting (cf. hydrocarbons 1-5). Introduction of a methyl group into the hexadecane molecule here lowers the melting point by  $57^{\circ}$  and a second methyl group lowers it another  $40^{\circ}$ . Aliphatic and aromatic hydrocarbons behave differently, as shown in Table 8, which compares benzene, toluene, and the xylenes. The viscosity-temperature behavior is very unfavorable when the straight carbon chain is completely or partially bound to the ring, as shown in Table 9.

It is evident here that increasing cyclization is accompanied by a sharp rise in viscosity and simultaneous impairment of viscosity-temperature behavior. Hydrocarbon No. 7 is interesting. We next turned our attention to the manner in which the results of this troublesome and tedious synthetic work could be applied commercially. The cracked wax polymerization process always yields a mixture of olefins the composition of which cannot be influenced.

We were led to consider ethylene. Dr. Otto had formerly shown that ethylene can be polymerized to normal butylene in the presence of small quantities of boron fluoride. We believed that, by using a more powerful catalyst, we could succeed in polymerizing ethylene still further to longer carbon

skeletons with long side chains. By using chemically pure ethylene with aluminum chloride as catalyst, we succeeded in obtaining a polymer which combined good viscosity-temperature behavior with good low-temperature characteristics (viz., low pour point). Thus, the Ethylene Lubricating Oil Synthesis was originated.

In the field testing of Ethylene Lubricating Oil it appeared that lubricating quality was not always satisfactory under extreme conditions. It is well known in the petroleum industry that the lubricating qualities of mineral hydrocarbon lubricating oils can be improved by the addition of fatty oils. However, fatty oils, which are esters of glycerol with high-molecular fatty acids, have the disadvantage of being extraordinarily sensitive to heat. It was supposed that this thermal instability resulted from the sensitivity of the secondary hydroxyl group of the glycerol. Trimethylolethane was supplied to me by the director, Dr. Giesen. The esters prepared from this together with Leuna carboxylic acids showed very good thermal stability. It was also possible to prepare esters which would meet the severe thermal demands of aircraft engines. Consequently, I traveled to Leuna and the relationship between the chemical constitution and properties of esters was investigated on a broad basis in cooperation with Dr. Löwenberg, Dr. Metzger, Dr. Ganicke, Dr. Heidingger, and Fräulein Dr. Rössig.

Table 10 shows esters formed from tri- and tetra-hydroxy alcohols esterified with various acids. First, let us compare the esters of normal octanoic acid. It appears that there is no difference between trimethylolethane and trimethylolpropane in regard to magnitude of viscosity and viscosity-temperature behavior, but there is considerable difference in low-temperature behavior (i.e., pour point), the ester of trimethylolpropane being superior to that of trimethylolethane by 61°. Glycerol is equivalent to both alcohols in regard to viscosity-temperature behavior; however, the magnitude of viscosity is smaller and the pour point considerably higher than for trimethylolpropane but lower than for trimethylolethane. Pentaerythritol gives an ester of appreciably higher viscosity, still higher pour point, and somewhat better viscosity-temperature behavior. It is very interesting to compare the esters of the four alcohols with a branched-chain acid, namely, 2-ethylhexanoic acid. The pour points of these four esters are all very low. There is no difference here between trimethylolethane and trimethylolpropane. The ester of glycerol has the lowest viscosity, that of pentaerythritol again the highest viscosity and similarly the best viscosity-temperature behavior. If, instead of 2-ethylhexanoic acid, the mixture of carboxylic acids is taken which is formed by the alcohol fractions from isobutyl alcohol boiling at 200-250°C, esters are obtained which are equivalent to those mentioned above in regard to viscosity behavior but not so favorable in regard to pour point. The pour point of the glycerol ester is remarkable. Esters of this type can be used in the coatings industry as softeners and in the electrical industry as switch oils. It is very interesting to observe the effect of incomplete esterification of these polyalcohols on viscosity-temperature behavior. These relations are shown in Table 11.

It is evident that, for trimethylolethane as well as pentaerythritol, the viscosity becomes higher and the viscosity-temperature behavior becomes poorer, the more free hydroxyl groups are present in the ester. This is

altogether understandable, for free hydroxyl groups cause a strong association of the ester molecules. All the alcohols are well known to be strongly associated. It is interesting that this association, i.e., formation of molecular complexes, proceeds altogether uniformly as shown in experiments conducted at Halle by Prof. Wolff and coworkers at my suggestion. Equal numbers of 1-, 2-, 3-, 4-, and up to 12-fold molecules are present in the whole mass. The investigation of esters of dihydroxyglycols is reviewed in Table 12. Ethylene glycol, tetramethylene glycol, hexamethylene glycol, methylhexamethylene glycol, and dimethylolpropane were investigated. It appears that, in the case of the esters of the straight-chain glycols with normal octanoic acid, there is an increase in viscosity and a decrease of the  $m$ -value (i.e., improvement in viscosity-temperature behavior) with increasing molecular weight. It is interesting that the pour point is lowered with methylhexamethylene glycol and dimethylolpropane. The influence of the methyl group is again noticeable here, as was already seen in the case of the hydrocarbon, hexadecane. The pour point is very favorably affected when isooctanoic acid or leuca carboxylic acid is employed instead of normal octanoic acid. However, the viscosity-temperature behavior is somewhat less favorable with these branched-chain acids.

A study of the esters of adipic and methyladipic acid is presented in Table 13. It is interesting to compare the esters of normal octanol and isooctanol. The latter has outstanding low-temperature behavior (pour point) because of the influence of the ethyl side chain. The effect of the methyl group is seen to be quite analogous on comparing cyclohexanol with methylcyclohexanol. Both these esters show higher viscosity and less favorable viscosity-temperature behavior than do the octanol esters. This is quite in agreement with the research on hydrocarbons. The cyclization of the carbon chain of the  $C_{28}$  hydrocarbon (cf. Table 9) may be recalled. The esters of methyladipic acid are only insignificantly different from the corresponding ones of adipic acid in regard to viscosity-temperature behavior, but are partially more favorable to an appreciable extent in regard to low-temperature behavior. Especially interesting from a practical viewpoint is the cyclohexanol ester of methyladipic acid. This finds application as a watch or clock oil, for it does not spread on metal surfaces but stays together in drops. Furthermore, it has an outlet as an additive in our aircraft hydraulic oil. The influence of the methyl group in dicarboxylic acids is exhaustively treated in Table 14. Let us compare the normal octanol and normal dodecanol esters of  $\alpha$ - and  $\beta$ -methyladipic acid with those of adipic acid. It is striking here that the esters of  $\alpha$ -methyladipic acid are consistently somewhat less favorable in regard to viscosity-temperature behavior than those of  $\beta$ -methyladipic acid. This is a striking example of the importance of the position of the side chain in the molecule. If the acids are esterified with branched-chain alcohols as, for example, our leuca alcohols or the alcohols which are obtained by applying the "Oxo" process to diisobutylene, esters are obtained of very outstanding low-temperature behavior. The esters of sebacic acid are especially noteworthy for they combine good pour point with outstanding viscosity-temperature behavior and consequently excel the esters of adipic acid. The ester of  $\beta$ -methyladipic acid with leuca alcohols finds an outlet in the preparation of motor oils suitable for low-temperature operation and axle oils; some were also found suitable as softeners for Igelite (resin or plastic?).

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\* Treatment with CO and H<sub>2</sub>.

The effect of increase in molecular size on viscosity-temperature behavior is shown in Table 15. The polyhydroxy alcohols were esterified both with normal octanoic acid and with long-chain semi-esters of adipic acid and Leuna alcohol fraction boiling from 140° to 180° (i.e., largely C<sub>6</sub> and C<sub>7</sub> alcohols). It appears that the latter esters are appreciably more viscous and somewhat more favorable in regard to viscosity-temperature behavior than are the esters of normal octanoic acid. It is quite understandable that the low-temperature behavior of this ester (as shown by pour point) should be outstanding, since the branched-chain Leuna alcohol is incorporated in the semi-ester. Furthermore, the lubricating qualities of esters of this type are very good. They have found a practical application as cutting oils. It is also possible to lengthen the straight chain of the molecule by ethoxylating an alcohol.

Results of the investigation of this subject are given in Table 16. First, the iso-C<sub>9</sub>-alcohol mixture obtained by the "Oxo" process on diisobutylene was employed as the alcohol. The ethoxylation was carried out by introducing ethylene oxide into the anhydrous alcohol. It is important here that all the alcohol molecules take up ethylene oxide uniformly. This uniform distribution of ethylene oxide is possible only through the agency of boron fluoride as catalyst. It is evident from Table 16 that the viscosity rises and that the viscosity-temperature behavior improves with increasing ethylene oxide content. On the other hand, low-temperature behavior becomes poorer the more ethylene oxide is taken up. It is very interesting to compare the products from Leuna alcohol treated with two moles of ethylene oxide and esterified with adipic, methyladipic, and sebacic acids. The low-temperature behavior of these three esters is exactly similar; the viscosity rises and the viscosity-temperature behavior improves in the order: adipic, methyladipic, and sebacic acid. Here, too, the sebacic acid ester is the most favorable. Unfortunately, these esters have the disadvantage that they are poorly miscible with hydrocarbon oils or even completely immiscible when they contain much ethylene oxide. More than one mole of ethylene oxide must not be taken up; with two moles of oxide miscibility with hydrocarbon oils is already lost at room temperature. However, this ester is completely miscible at higher temperature (e.g., 80°). With still higher molar proportions of oxide, even the miscibility at higher temperatures is lost.

After we had studied the relation between the constitution of esters and their viscosity characteristics to some extent, we proceeded to investigate the relation between their constitution and lubricating properties. For this purpose, we made use of an apparatus developed at the technical testing station at Oppau, the so-called Chain Apparatus. As shown in Figure 17, this consists of a chain loaded by a weight, the chain being pressed against the lower half of the circumference of a roller. Chain and roller are immersed in the test oil which can be heated electrically. The chain is pulled in the direction of rotation of the roller more or less strongly, depending on the lubrication by the oil, and consequently causes a corresponding stress on the scale. Since there is only point contact between separate chain links and the roller and since the circumferential velocity is kept low, the apparatus operates in the region of boundary lubrication. In Figure 18 are presented some results

obtained on this apparatus. Curves 1, 2, and 3 are values for adipic acid esters of the straight-chain alcohols, butanol, octanol, and dodecanol. It is evident that the coefficient of friction falls and the dependence of coefficient of friction on temperature steadily improves with increasing molecular weight. If the adipic acid in these esters is replaced by methyladipic acid (so as to give Esters 4 and 5), it is evident that the coefficient of friction for the methyladipic acid ester is always higher than for the corresponding adipic acid ester. This influence of the methyl group is again confirmed on comparing Esters 2 and 6, as well as 6 and 7 (cf. Figure 19). The right-hand plot is interesting, which gives wear values measured by a hard metal disc pressed against a steel plate. It is evident here that the ester which gives the highest coefficient of friction also gives the lowest wear value.

Figure 20 shows the same result. Here the esters of dihydroxyglycols are compared with each other. The ester with the longest carbon chain has the lowest coefficient of friction and, again, the highest wear value.

Figure 21 again shows a sharp decrease in coefficient of friction with increasing molecular weight of the ester (compare No. 25 with 11, 12, 13, and 16). The temperature dependence becomes steadily more favorable. In the case of Ester 16, a small decrease in coefficient of friction with increasing temperature was observed. Furthermore, it is interesting to compare 11 and 12. The branched-chain acid again shows the higher coefficient of friction and the stronger dependence of coefficient of friction on temperature. It is also interesting that the coefficient of friction is only slightly increased by incomplete esterification and the temperature dependence is not affected at all (cf. 17 and 15). In the wear experiments, the order of rating of the esters is again just the reverse as for coefficient of friction. Also in the case of the still higher molecular esters, it is confirmed that the coefficient of friction decreases and the  $\mu$ -temperature curve becomes flatter with increasing molecular weight, as shown in Figure 22.

This interesting reversal of behavior between lubricating quality, as characterized by coefficient of friction, and wear arises from the force with which molecules are held on the surface. The work which must be expended in tearing loose a 1-sq. cm. cross-section of the liquid from the interface is defined as energy of adhesion. It can be determined by measuring the interfacial tension  $\gamma$  and surface tension  $\sigma$  of both phases. The Dupr e rule holds here:  $H = \sigma_1 + \sigma_2 - \gamma_{12}$ . Prof. Wolff at Halle investigated numerous materials with reference to their energies of adhesion at my suggestion. Some results of this investigation are shown in Table 23.

With reference to hydrocarbons, it is interesting to note the behavior of benzene, which is held appreciably more firmly on mercury than is its hydrogenation product, cyclohexane. In the series of alcohols, an increase of energy of adhesion is observed with increasing length of the carbon chain. It is noteworthy that branching of the carbon chain causes a diminution in energy of adhesion. In the case of acids, the energy of adhesion is altogether

independent of molecular size. This results from the fact that dimeric molecular association occurs with all acids. Greater than two-fold molecular complex formation occurs only in the case of formic acid. With esters, just as in the case of alcohols, we observed an increase in the energy of adhesion with increasing molecular weight of the alcohol constituent. It is noteworthy here that branching of the alcoholic carbon chain does not entail an increase in the energy of adhesion. The reason for this difference in behavior as compared with the straight alcohols probably lies in the manner in which the molecules are oriented at the interface. There are two possibilities here: either they stand upright with their carbon chains perpendicular to the interface, or they lie down tangentially. The question as to which orientation is favored for a given type of material depends both on the steric location of the dipole group in the molecule and on the position and magnitude of the permanent dipole within the group.

The energies of adhesion are naturally dependent not only on the lubricant but also on the other phase in contact with it. The differences between energy of adhesion for various materials against an aqueous and against a metallic surface are collected in Table 24. It is evident that there is a large difference between water and mercury. The several materials adhere to mercury on the average two to three times as strongly as to water. The adhesive resistance can be calculated from the energy of adhesion.

Table 25 gives the corresponding values for hydrocarbons, alcohols, and acids. It is again evident that the adhesive resistance increases with increase in degree of unsaturation for hydrocarbons, with increase in carbon chain length for alcohols, and is independent of the molecular size for acids. These adhesive resistances, which are a measure of the force required to tear away a surface of 1 sq. cm. cross-section, correspond to the internal resistance to rupture within the liquid or the metal.

The latter is calculated from the interfacial tension; it denotes the resistance to rupture. The magnitude of these values for liquids is remarkable. The rupture of a liquid organic acid requires the same force or perhaps even a greater force than does the rupture of a metal such as brass or iron. Without further ado, this fact explains the reversal of behavior between coefficient of friction and wear. The greater the adhesive resistance of a lubricant, the stronger is the lubricating film and therefore the smaller the coefficient of friction but, on the other hand, the larger is the force with which the liquid molecules can tear a metal atom out of its surface. Consequently, when we wish to obtain low wear, we should not develop lubricants which show extraordinarily high adhesive resistance, but rather we should only approach an optimum. In order to arrive at this goal, we must direct our attention not so much at the dipole forces of the molecule, but rather at the dispersion forces of the molecule which arise from the specific quantum binding of the carbon chain. However, not only the lubricant but also the other phase (namely, the metal) is responsible for wear.



Figure 28 shows the different behavior of various metals against the same lubricant. A material (e.g., polyether alcohol IK-2200) can have extraordinarily strong antiwear properties against red brass, but cause wear of soft metal to such an extent that one can almost say that the metal is dissolved by the liquid. Also, a straight mineral oil (e.g., Oil K7) behaves very differently against various metals.

This difference in behavior of oils against various metals is naturally also reflected in actual lubrication. If consideration is given to the various states of lubrication of the journal bearing in Figure 27, the chemical constitution of the lubricant becomes important in the region where the speed of rotation is low and the loading correspondingly high. This is the range of partial lubrication (quasi-hydrodynamic) and boundary lubrication.

The difference in behavior of various bearing metals against the same oil in a state of boundary lubrication is shown in Figures 28, 29 and 30. These experiments were carried out by Prof. Heidebroeck at Dresden. It is evident that the transition point from hydrodynamic to boundary lubrication at the same degree of loading varies with the nature of the bearing metal and of the oil. It is a question here of the action of the boundary surface forces in thick films of liquid. That orientation must extend from the boundary surface into fairly deep layers of the liquid appears still more probable on comparing the action of two different bearings with the same oil (cf. Figure 31). It is evident that, with a given bearing clearance, different oil pressures must be employed for passage of a definite quantity of oil per unit time, depending on the nature of the bearing material. Aside from these forces which originate at the boundary surface, the state of lubrication is influenced by processes determined by the structure of the liquid.

In Figure 32 (illegible) are demonstrated some results which professor Heidebroeck obtained on a gear-test apparatus. This consists of two gears carefully mounted on bearings in which is incorporated a quartz gauge sensitive to pressure. This makes it possible to determine on an oscillograph the slightest vibrations which are caused by unevenness of the gear-tooth surfaces. In this apparatus the tooth surfaces are lubricated with an accurately determined quantity of lubricating oil (measured to 1cc.) and then the time measured which elapses until the lubricant film fails, as characterized by the appearance of rust spots on the tooth surfaces (so-called "frictional oxidation"). At the same time, the state of vibration of the gears is picked up on the oscillograph and the amplitude of these vibrations is measured. In this manner, seven oils of different viscosity and different composition were investigated. It is evident that the life time, i.e., the time until the onset of frictional oxidation, is very different and bears no relation to the magnitude of viscosity. The same is true for the amplitude of vibration, as in the case of Oils 13, 14, and 15. Three esters are involved here. No. 13 is a polybutylene glycol; No. 14 is a polyester from two moles of trimethylolthane and 1 mole of adipic acid esterified with Ieuna carboxylic acid; No. 15 is the same polyester except

that higher fatty acid obtained from the oxidation of wax at Oppau was used instead of leuca carboxylic acid. It is evident that 1 cc. of Ester No. 14 shows an extraordinarily high film life while Ester No. 15 is characterized by a very small amplitude of vibration on the oscillograph. This ester thus gave very quiet operation of the gears. Oils 5, 6, and 7 are high-molecular ethylene polymers with significantly greater viscosity than Ester No. 15, but nevertheless the vibration amplitudes for these highly viscous oils are twice as high as for the appreciably more fluid Ester No. 15. The magnitude of viscosity, i.e., the size of the molecules, is thus without significance for the quiet operation of a gear machine. Molecular structure is the determining factor here. Oil No. 15 is a voltolized fatty oil of considerable repute for lubricating journal bearings. It has no advantage for roller bearing lubrication.

The oscillogram for the oils mentioned above is shown in Figure 33 (missing). The very quiet operation with Ester No. 15 is very noticeable in contrast to the rough operation with voltolized fatty Oil No. 12, which is 7 times as viscous. We succeeded in so directing the course of ethylene polymerization that a polymer was obtained which behaves like Ester No. 15 in damping vibrations and consequently suppressing noise.

In Figure 34 (illegible) are shown sound measurements which F. Krupp made on oil of this type. It is also very interesting to note the action of such damping oils on the course of frictional phenomena in a journal bearing. This same oil (investigated by F. Krupp) was also studied by Prof. Heidebroeck in a journal bearing.

In Figure 35 (illegible) presents the results of this investigation. Five different oils were tested here. Our damping oil is Oil K-I. Oil K-II is also an ethylene polymer of low viscosity. The completely different type of behavior of Oil K-I, which maintains the hydrodynamic state of lubrication even at the lowest speeds, is very evident. It is shown in the lower part of the figure that mixtures of Oil K-I with K-II can also be prepared which avoid boundary lubrication conditions even at low speeds.

Figure 36 illustrates the influence of temperature on the course of frictional phenomena in a journal bearing. Friction decreases with increasing temperature, whereas viscosity becomes lower. It is significant that Oil K-I does not give boundary lubrication even at the lowest speeds, as shown in the lower figure. The effect of temperature on the course of frictional phenomena, or rather on lubrication, has presented us with a number of technical problems during the last two years of the war. The first of these problems was the lubrication of arms at the very low temperatures encountered by the Luftwaffe (German Air Force) at high altitudes.

In Table 37 (illegible) is shown the effect of magnitude of viscosity on the firing of a Luftwaffe machine gun at very low temperatures. The task given us was to prepare fluid oils which would make possible satisfactory operation of machine guns at full firing speed even at  $-60^{\circ}$ . As shown in this table, we succeeded in doing so with Oils 494 and 495. To this end, we

found it necessary to search for materials which, even though of very low viscosity, could absorb the high pressures at different bearing points.

In Table 38 (illegible) is shown the relation between the chemical constitution of various materials and their viscosity, as well as their efficiency of lubrication in machine guns. The latter is characterized first by the time required for 50 shots and second by the number of shots which can be made with one lubrication of the gun. It is evident that speed of firing and total number of shots are very different, according to the structure of the various materials. The last material, No. 442, achieved a solution to the problem. Here we arrived at a material which is obtained on treating the xanthate of amyl alcohol with sulfur monochloride. This material gives a golden yellow oil which contains about 50% of sulfur; it is, so to speak, a liquid form of sulfur. This has given valuable service not only in the field of lubrication but has also found application in the field of coatings. For rubber coatings (the so-called Pervinan coatings), the problem was to prepare a liquid coating material which could be vulcanized and spread. Since this material (called Nesulfol) is soluble in all paint solvents and, on firing the coating, decomposes with the separation of very reactive sulfur, it is now very easy to vulcanize Pervinan. A fortunate decision of the director, Dr. Giesen, may be noted here, namely, to add a coatings laboratory to the lubricants laboratory. Both fields pertain to the application of research on surface phenomena and on the structure and behavior of liquids.

The performance of Nesulfol in the lubrication of machine guns is shown in Table 39. It is noteworthy that Nesulfol functions differently in esters and in hydrocarbon oils (cf. 463 and 469). Hydrocarbon oils demand a greater addition of sulfur in order to obtain good firing efficiency, as shown on comparing 469 with 495. For practical purposes we therefore found it necessary to standardize on a 50:50 mixture of ester and hydrocarbon. This product was employed by the Luftwaffe in increasing quantity since January 1941. We began with 5 metric tons per month and have today reached 50.

A second outlet for our esters was found in the Reichsbahn (railroads). Here it was a matter of preparing axle oils capable of operation at the low temperatures encountered in the East, viz., to develop axle oils which exhibit good capillary flow in the lubricating pads of freight cars at  $-40^{\circ}$ ; the satisfactory lubrication of the axle bearings and consequently the coasting speeds of the freight cars in the freight yards depends on the capillary properties in the lubricating packing which is made of artificial silk fiber. If, in winter time, the freight cars do not coast as far as necessary, then uncoupling and coupling them requires a large number of locomotives which are not available for this purpose. Axle oils which have thus far been used on the German railroads consist of by-products from petroleum refineries.

Table 40 shows the composition of the mineral axle oils. It is evident that they contain only 50 to 60 per cent of true lubricating oil hydrocarbons, the remainder being undesirable extraneous material of various chemical composition. Table 41 shows the viscosity-temperature behavior of these oils. It appears that there is a large difference in magnitude of

viscosity at  $-20^{\circ}$  and  $-30^{\circ}\text{C}$ . It is further evident on comparing the mixtures of oils with each other (cf. 6 and 7, or 8, 9, and 10) that the oils have a very strong mutual effect on each other. We first attempted to thin the oils by addition of an ester and thus improve their behavior at low temperature. In this way, we were able greatly to diminish the viscosity at low temperature; however, the capillary behavior in the lubricating packing could not be improved to the desired extent by this means, as shown in Table 42. Addition of gas oil was better here, as shown especially by the capillary behavior at  $-10^{\circ}$ . The functioning of the gas oil is related to the fact that it is well able to dissolve wax and other foreign bodies such as resins and asphalt whereas the ester is not able to do this. However, in the temperature range in which the ester is miscible with hydrocarbons and these materials, its higher capillary forces became noticeable as shown by the increase in capillary flow at  $50^{\circ}\text{C}$ . We have thus solved the problem by the method of preparing a mixture of about 40 parts of an adipic acid ester with 60 parts of a synthetic hydrocarbon oil. This mixture was completely homogeneous even at low temperatures, as shown in Table 43 (illegible) by the linear curve for viscosity against temperature of our  $\gamma$ -Axle Oil in comparison with natural axle oil. The necessary hydrocarbon components are obtained by polymerizing those hydrocarbons which are formed on the decomposition of the aluminum chloride sludge from the production of SS 906. According to a decree of Reichsminister Dornmüller, all cars on the German railroads shall be changed over to this oil from March of last year until the year 1945. This change will have the result that, in the German petroleum industry, about 50,000 metric tons per year of petroleum products will be made available for other purposes.

Finally, we come to the most important outlet for the synthesis, the field of motor lubrication, which was the original incentive for all our work.

In Figure 44 (illegible) are shown the effects of adding 25% of ester to a hydrocarbon aircraft oil, namely, both an increase in useful lifetime of the oil and a sharp reduction in ring wear. A significant improvement in running time was obtained by the addition of ester also in the case of synthetic oil No. SS 904, as shown in Table 45 (illegible). It is important that, on the addition of ester, an inhibitor is also present, as demonstrated by comparing Experiments 475 and 560. We had determined the significance of the addition of inhibitor 8 years before entirely in engine tests. Only recently did we succeed in understanding the action of these materials somewhat more thoroughly.

In Figure 46 is shown the action of oxygen on our synthetic oil SS 906. These experiments, which were begun by Dr. Fiedler and continued by Dr. Maichle, demonstrate that Oil SS 906 absorbs oxygen with the formation of peroxide. Simultaneously, with increasing peroxide content, the iodine number falls off, the acid number increases, and the viscosity increases very sharply. The latter especially is a very undesirable phenomenon when the aim is to develop an oil which has good low-temperature behavior; for, in this case, it is required that the viscosity does not change in service. If there is such a viscosity increase on use (i.e., by the action of oxygen), then the desirable low-temperature properties are lost. We must therefore seek materials which

avoid or diminish the cause of the thickening, that is, the formation of peroxides. We found such a material in silver which, as shown in Figure 47, very strongly diminishes oxygen absorption and the accompanying formation of peroxides or stops it completely. We use this silver in the form of a salt of diisobutylene-phenolsulfide. It was shown in this investigation that not every organic silver compound has the same effectiveness.

The dependence of viscosity increase through oxidation on the inhibitor concentration is shown in Figure 48. It is evident that addition of 0.2% reduces the viscosity increase by about half. In engine tests on this inhibitor, the length of the run was increased by about 100% and simultaneously lacquer deposition on the piston skirts considerably reduced. At the same time, the viscosity increase of the oil while in use was likewise very much reduced. The decrease in lacquer formation in these engine tests is especially important; we know that lacquers are materials of high oxygen content. We may now surmise that the primary cause of their formation is the action of peroxides. From a practical point of view, the decrease in lacquer formation results in increased overhaul time for the engines, thus accomplishing a saving in ground personnel.

One goal of lubricating oil research is especially to develop oils which do not cause contamination of any part of the machinery and consequently permit the lubricant to be regarded as a structural element of the engine. Here, research on inhibitors in the field of organic catalysis can provide decisive contributions to the war effort.

Figure 49 (illegible) shows the present status of development of aircraft oils for low temperatures. The goal here is to produce an oil which has a viscosity no greater than 2000 °E (Engler) at -40°. Figure 50 (illegible) shows the present status of development in regard to motor oils. With the oils represented here an SS Division was able to travel in the East during the past winter without any difficulties due to low temperatures. The problem presented to us by the automobile industry, which we should attempt to solve, is to produce an oil with a maximum viscosity of about 1000 °E at -40°C.

In Figure 51 (illegible), is shown the relation between viscosity-temperature behavior and the adhesive resistance. The latter is a measure of the force which must be employed in order to set in motion a shaft mounted on bearings in the oil at low temperature. This was measured on an apparatus developed at the Oppau technical test station and universally introduced by the Luftwaffe. It is evident from the figure that the adhesive resistance increases sharply with increase in viscosity. If it is desired to obtain with highly viscous oils the low adhesive resistance which is characteristic of low-viscosity oils, then the viscosity-temperature behavior characterized by the slope factor  $m$  must be very greatly improved. Values of 3.0 and less must be reached; at present we have obtained values of 3.2.

In Figure 52 (illegible) are presented the pertinent adhesive resistance values for our present low-temperature motor oil. It is evident that this has the same adhesive resistance at  $-35^{\circ}$  as the best mineral Wehrmacht (ground force) winter oil up to now. We have thus come very close to the goal which was set.

These development problems are now made difficult during the war because the raw materials which are required steadily become scarcer and scarcer. Therefore we found it necessary to start synthetic work for solving the problems of raw materials. This was recently accomplished by resumption of the work on copolymerization which was begun in the year 1930. We had then been able to show that it is possible to refine a dewaxed, deasphalted, and deresined petroleum lubricating oil fraction by treating it with the crude cracked-wax polymer which still contains aluminum chloride. The reactive hydrocarbons present in the mineral oil react with the cracked-wax polymer in such a manner that they are alkylated, polymerized, and isomerized; thus a copolymer is obtained which is superior to a simple physical mixture of synthetic product and mineral oil raffinate in regard to engine performance, as shown in Table 53. During the last year we have extended this process to ethylene polymerization with the same results, and now plan to construct a refinery at Moosbierbaum in which the processing of natural products will be combined with that of synthetic products on a plant scale. Thus the process discovered in the year 1930 and patented is finally put into practice. Furthermore, in constructing this refinery at Donau we desire that not only shall nature and synthesis be combined in the field, but also that natural products shall always be utilized more completely in regard to fuel production.

In the following and final figure is briefly summarized the influence which the lubricants research of our organic section has thus far achieved on development in production. It is evident from Figure 54 that, except for two materials, all the products of our section could be usefully applied in the field of lubricants.

The "taunting and deceptive pranks" of chemistry have been turned to good advantage in research work conscious of a definite goal in the field of lubricants. For the future, we hope that the research and development work thus far accomplished in the welfare of our fatherland can be continued, for the only recompense of the work was to succeed in solving many war problems.

Table 1

Olefin	Yield, %	Viscosity		V. I.
		38°	99°	
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH=CH}_2$	85	34.4	2.91	99
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH=CH-CH}_2\text{-CH}_3$	45	5.60	1.42	24
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH=CH}_2$	70	38.70	3.56	114
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH=CH}_2 \\   \\ \text{CH}_3 \end{array}$	85	387.0	13.20	98
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-C=CH}_2 \\   \\ \text{CH}_2\text{-CH}_3 \end{array}$	39	6.16	1.42	14

/C8

Figure 2 Polymerization Diagram for n-Octylene

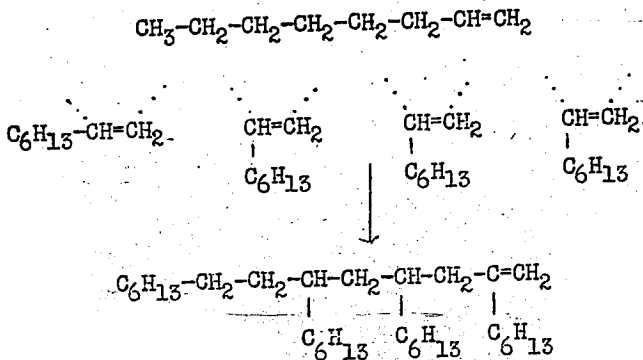




Figure 3 Illegible  
Table 4 Illegible  
Table 5 Illegible  
Table 6 Missing

Table 7

Empirical Formula	M.W.	Empirical Structure	Spec. Gr. 20°C	Viscosity in cs.				m	Vis. Pole Ht.	V.I.	Melt-ing Pt., °C
				20	38	50	99				
C <sub>16</sub> H <sub>34</sub>	226	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>14</sub> -CH <sub>3</sub>	0.7753	4.39	2.94	2.42	1.30	3.34	0.1	—	18
C <sub>16</sub> H <sub>34</sub>	226	n-C <sub>8</sub> H <sub>17</sub> -CH-CH <sub>2</sub> -C <sub>6</sub> H <sub>13</sub>   CH <sub>3</sub>	0.7758	4.20	2.92	2.0	1.28	3.32	0.1	—	-38.8
C <sub>16</sub> H <sub>34</sub>	226	n-C <sub>6</sub> H <sub>13</sub> -CH-CH-C <sub>6</sub> H <sub>13</sub>   CH <sub>3</sub> CH <sub>3</sub>	0.7811	4.22	2.78	2.21	1.23	3.45	0.1	—	-80
C <sub>16</sub> H <sub>34</sub>	226	n-C <sub>4</sub> H <sub>9</sub> -CH-CH <sub>2</sub> -CH <sub>2</sub> -CH-C <sub>4</sub> H <sub>9</sub>   C <sub>2</sub> H <sub>5</sub>   C <sub>2</sub> H <sub>5</sub>	0.7823	3.70	2.55	2.09	1.10	3.58	0.06	—	ca. -80
C <sub>16</sub> H <sub>34</sub>	226	n-C <sub>4</sub> H <sub>9</sub> -CH-CH <sub>2</sub> -CH-CH <sub>2</sub> -CH-CH <sub>3</sub>   C <sub>2</sub> H <sub>5</sub>   C <sub>2</sub> H <sub>5</sub>   C <sub>2</sub> H <sub>5</sub>	0.7791	3.58	2.46	2.02	1.07	3.62	0.04	—	ca. -80
C <sub>24</sub> H <sub>50</sub>	338	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>22</sub> -CH <sub>3</sub>	0.7746 60	14.9	(8.98)	(6.63)	2.1	(3.2)	(0.7)	(224)	51
C <sub>24</sub> H <sub>50</sub>	338	n-C <sub>6</sub> H <sub>13</sub> -CH-CH <sub>2</sub> -CH <sub>2</sub> -CH-C <sub>6</sub> H <sub>13</sub>   C <sub>4</sub> H <sub>9</sub>   C <sub>4</sub> H <sub>9</sub>	0.8020	16.96	9.03	6.28	2.32	3.89	1.3	117	ca. -66
C <sub>24</sub> H <sub>50</sub>	338	n-C <sub>5</sub> H <sub>11</sub> -CH-CH <sub>2</sub> -CH <sub>2</sub> -CH-C <sub>5</sub> H <sub>11</sub> -n   n-C <sub>5</sub> H <sub>11</sub>   n-C <sub>5</sub> H <sub>11</sub>	0.8114	18.09	9.4	6.50	2.34	3.95	1.42	88	—
C <sub>24</sub> H <sub>50</sub>	338	n-C <sub>5</sub> H <sub>11</sub> -CH-CH <sub>2</sub> -CH <sub>2</sub> -CH-C <sub>5</sub> H <sub>11</sub> -n   i-C <sub>5</sub> H <sub>11</sub>   i-C <sub>5</sub> H <sub>11</sub>	—	23.2	10.85	7.43	2.41	4.20	2.05	26	—
C <sub>24</sub> H <sub>50</sub>	338	n-C <sub>4</sub> H <sub>9</sub> -CH-CH <sub>2</sub> -CH-CH <sub>2</sub> -CH-C <sub>4</sub> H <sub>9</sub>   C <sub>2</sub> H <sub>5</sub>   C <sub>2</sub> H <sub>5</sub>   C <sub>2</sub> H <sub>5</sub>	0.8119	18.27	9.1	6.28	2.27	4.04	1.58	89	ca. -66

Table 8 Constitution and Melting Point

Benzene	+ 5.5°
Toluene	-95°
Ethylbenzene	-94°
m-Xylene	-54°
o-Xylene	-29°
p-Xylene	+13°
<b>Cetanes:</b>	
$\text{CH}_3-(\text{CH}_2)_{14}-\text{CH}_3$	+18°
$\text{CH}_3-(\text{CH}_2)_7-\underset{\text{CH}_3}{\text{CH}}-(\text{CH}_2)_5-\text{CH}_3$	-39°
$\text{CH}_3-(\text{CH}_2)_5-\underset{\text{CH}_3}{\text{CH}}-\underset{\text{CH}_3}{\text{CH}}-(\text{CH}_2)_5-\text{CH}_3$	-80°
$\text{CH}_3-(\text{CH}_2)_5-\underset{\text{C}_2\text{H}_5}{\text{CH}}-\text{CH}_2-\text{CH}_2-\underset{\text{C}_2\text{H}_5}{\text{CH}}-(\text{CH}_2)_3-\text{CH}_3$	-80°
$\text{CH}_3-(\text{CH}_2)_5-\underset{\text{C}_2\text{H}_5}{\text{CH}}-\text{CH}_2-\underset{\text{C}_2\text{H}_5}{\text{CH}}-\text{CH}_2-\underset{\text{C}_2\text{H}_5}{\text{CH}}-\text{CH}_3$	-88°



Table 10

Esters of Tri- and Tetra-Hydroxy Alcohols	Spec. Gr. 20°C	Viscosity in cs., °C				Pour Point °C	
		20	38	50	99		
$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CH}_3-\text{C}-\text{CH}_2\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array} + \text{n-Octanoic Acid}$	0.944	36.20	17.75	11.96	3.86	3.58	-8
$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CH}_3-\text{CH}_2-\text{C}-\text{CH}_2\text{OH} \\   \quad   \\ \text{CH}_2\text{OH} \quad \text{CH}_2\text{OH} \end{array} + \text{n-Octanoic Acid}$	0.948	37.00	18.00	12.20	3.96	3.57	-69
$\text{HO}-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_2\text{OH} + \text{n-Octanoic Acid}$	0.940	25.54	12.97	8.98	3.20	3.57	-24
$\text{HO}-\text{CH}_2-\underset{\text{CH}_2\text{OH}}{\text{C}}-\underset{\text{CH}_2\text{OH}}{\text{C}}-\text{CH}_2\text{OH} + \text{n-Octanoic Acid}$	0.959	50.79	23.80	15.69	4.73	3.50	+ 7
Trimethylolmethane + 2-Octanoic Acid	0.948	49.30	20.90	13.5	3.84	3.88	-63
2-Ethylhexanoic Acid							
Trimethylolpropane + 2-Octanoic Acid	0.948	64.82	26.28	16.09	4.17	4.02	-58
2-Ethylhexanoic Acid							
Glycerol + 2-Octanoic Acid	0.952	40.27	17.39	11.10	3.21	4.11	-66
2-Ethylhexanoic Acid							
Pentaerythritol + 2-Octanoic Acid	0.966	145.7	52.01	29.94	6.37	3.91	-45
2-Ethylhexanoic Acid							
Trimethylolmethane + Leuna Carboxylic Acid mixture (200/250)	0.949	123.0	42.50	24.75	5.57	3.96	-48
Trimethylolpropane + Leuna Carboxylic Acid mixture (200/250)	0.958	144.7	50.20	28.60	6.30	3.97	-49
Glycerol + Leuna Carboxylic Acid mixture (200/250)	0.954	94.4	34.0	20.7	4.93	3.96	-60
Pentaerythritol + Leuna Carboxylic Acid mixture (200/250)	0.961	453.0	117.2	63.5	10.46	3.88	-31

Table 11

Esters of Tri- and Tetra-Hydroxy Alcohols Incomplete Esterification.	Spec. Gr. 20°C	Viscosity in cs., °C				m 20:99	Pour Point, °C
		20	38	50	99		
Trimethylolmethane + 3 Moles i-C <sub>13</sub> Acid	0.917	97.90	42.13	26.66	7.11	3.54	-28
Trimethylolmethane 2 Moles i-C <sub>13</sub> Acid	0.925	124.5	49.90	29.87	7.27	3.51	-27
Trimethylolmethane 3 Moles Leuna Carboxylic Acid	0.949	123	42.50	24.8	5.57	3.96	-48
Trimethylolmethane 2 Moles Leuna Carboxylic Acid	0.962	193	59.50	32.40	6.57	4.01	-44
Trimethylolmethane 1 Mole Leuna Carboxylic Acid	0.982	427	105	51.5	7.80	4.34	-33
Pentaerythritol 4 Moles i-C <sub>13</sub> Acid	0.929	279.50	71.10	42.80	10.00	3.27	-28
Pentaerythritol 3 Moles i-C <sub>13</sub> Acid	0.934	213.2	81.20	48.50	10.40	3.33	-27
Pentaerythritol 2 Moles i-C <sub>13</sub> Acid	0.951	339.0	114.9	64.50	11.70	3.50	-26

Table 12.

Esters of Dihydroxy Glycols	Spec. Grav. 20°C	Viscosity in cs., °C				m. 20:99	Pour Point, °C
		20	38	50	99		
HO-CH <sub>2</sub> -CH <sub>2</sub> -OH + n-Octanoic Acid	0.934	9.00	5.36	4.03	1.76	3.67	+18
HO-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH + n-Octanoic Acid	0.919	11.77	6.85	5.17	2.29	3.38	+13
HO-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH + n-Octanoic Acid	0.920	14.40	8.40	6.26	2.62	3.33	+ 9
HO-CH <sub>2</sub> -CH(CH <sub>3</sub> )-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH + n-Octanoic Acid	0.916	15.40	8.88	6.55	2.71	3.51	—
$\begin{matrix} \text{CH}_3 & & \text{CH}_2\text{OH} \\ & \diagdown & / \\ & \text{CH} & \\ & / & \diagdown \\ \text{CH}_3 & & \text{CH}_2\text{OH} \end{matrix}$ + n-Octanoic Acid	0.920	14.50	8.10	5.87	2.36	3.62	-35
Tetramethylene Glycol + 1-Octanoic Acid	0.936	12.80	6.89	4.88	1.98	3.86	<-72
Hexamethylene Glycol + 1-Octanoic Acid	0.929	16.60	8.68	6.18	2.37	3.73	<-72
Methylhexamethylene Glycol + 1-Octanoic Acid	0.915	18.20	9.20	6.50	2.48	3.70	<-72
Dimethylolpropane + 1-Octanoic Acid	0.920	17.60	8.77	6.05	2.16	4.13	<-72
Tetramethylene Glycol + 2-Ethyl Hexanoic Acid	0.980	22.00	11.80	8.2	2.94	3.64	<-72
Hexamethylene Glycol + 2-Ethyl Hexanoic Acid	0.926	23.53	12.20	8.60	3.20	3.44	<-72
Methylhexamethylene Glycol + 2-Ethyl Hexanoic Acid	0.922	29.60	14.80	9.97	3.40	3.63	<-72
Dimethylolpropane + 2-Ethyl Hexanoic Acid	0.930	32.90	15.40	10.00	3.21	3.90	<-59

Table 13

Esters of Dicarboxylic Acids with Branched-Chain and Cyclic Alcohols as Compared with Straight-Chain Alcohols	Viscosity in cs., °C			m 20:99	Pour Point, °C
	38	50	99		
Adipic Acid + n-Octanol	8.75	—	2.85	3.09	-10
Adipic Acid + i-Octanol = 2-Ethyl-Hexanol	7.85	—	2.26	3.43	←-72
Adipic Acid + Cyclohexanol	27.70	12.90	4.42	(3.24)	-40
Adipic Acid + m- and p-Methylcyclohexanol	5.95	17.60	4.64	3.76	-52
Adipic Acid + i-Hexanol-2-Ethyl-Butanol	—	—	1.77	3.65	←-72
β-Methyladipic Acid+n-Octanol	9.22	6.67	2.90	3.16	-36
β-Methyladipic Acid+i-Octanol	—	—	2.61	3.65	←-72
β-Methyladipic Acid+Cyclohexanol	—	—	—	3.95	-50
β-Methyladipic Acid+m- and p-Methylcyclohexanol	25.73	15.60	4.28	3.99	-46
β-Methyladipic Acid+i-Hexanol	—	4.77	2.02	3.72	←-72



Table 14

Esters of Dicarboxylic Acids	Spec. Gr. 20°C	Viscosity in cs., °C				m 20:99	Four Point, °C
		20	38	50	99		
Adipic Acid + n-Octanol	0.919	14.2	8.75	6.28	2.85	3.09	+10
Adipic Acid + n-Dodecanol	—	—	—	12.40	4.53	(3.05)	+56
α-Methyladipic Acid + n-Octanol	0.927	16.80	9.33	6.66	2.66	3.48	-32
α-Methyladipic Acid + n-Dodecanol	0.913	36.13	17.30	12.10	4.28	3.23	+16
β-Methyladipic Acid + n-Octanol	0.920	16.00	9.22	6.67	2.90	3.16	-36
β-Methyladipic Acid + n-Dodecanol	0.898	35.90	18.60	15.20	4.71	2.96	+10
Adipic Acid + Leuna Alcohol (100-250)	0.930	32.73	16.40	10.85	3.65	3.60	-69
α-Methyladipic Acid + Leuna Alcohol (100-250)	0.933	49.20	20.90	13.40	4.07	3.71	-60
β-Methyladipic Acid + Leuna Alcohol (100-250)	0.913	49.60	21.20	13.60	4.16	3.67	-59
Dimethyladipic Acid + Leuna Alcohol (100-250)	0.932	58.70	24.20	15.50	4.29	3.85	-37
Sebacic Acid + Leuna Alcohol (100-250)	0.916	44.10	20.70	13.90	4.45	3.48	-70
Adipic Acid + i-C <sub>9</sub> Alcohols from "Oxo" Process on Diisobutylene	0.918	24.00	12.70	8.70	3.21	3.43	<-72
β-Methyladipic Acid + i-C <sub>9</sub> Alcohols from "Oxo" Process on Diisobutylene	0.916	28.20	14.60	10.00	3.59	3.49	-70
Dimethyladipic Acid + i-C <sub>9</sub> Alcohols from "Oxo" Process on Diisobutylene	0.916	30.73	15.00	10.41	3.59	3.39	-60
Sebacic Acid + i-C <sub>9</sub> Alcohols from "Oxo" Process on Diisobutylene	0.911	38.35	19.50	13.40	4.71	3.20	-40

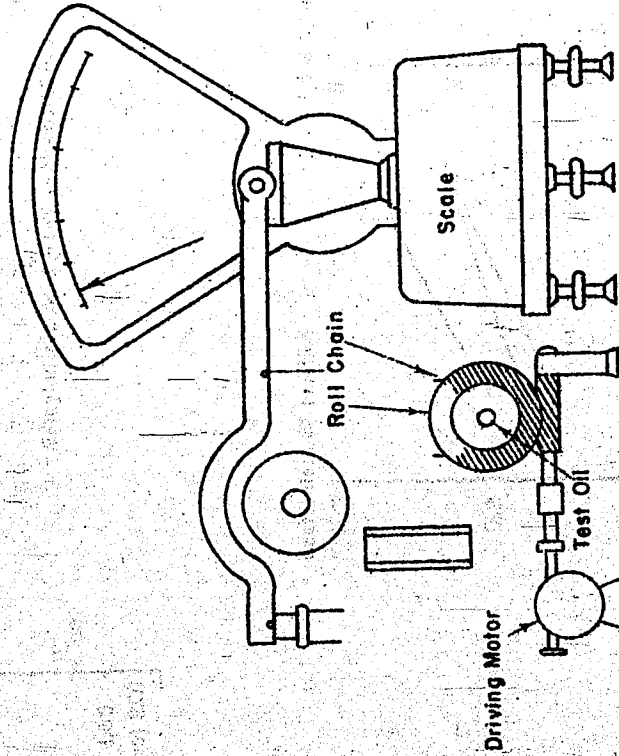
Table 15

Esters of Polyhydroxy Alcohols and Semiesters (HE) of Adipic Acid $\text{H}^{\text{OOC}}-(\text{CH}_2)_4-\text{COOH}$ R-Leuna Alcohol 140/180	Spec. Gr. 20°C	Viscosity in cs., °C				m 20:99	Pour Point, °C
		°C					
		20	38	50	99		
Ethylene Glycol + HE + n-C <sub>8</sub> Acid	0.992 0.984	43.53 9.00	20.10 5.36	13.30 4.03	4.30 1.76	3.48 3.57	-62 +18
Tetramethylene Glycol + HE + n-C <sub>8</sub> Acid	0.993 0.919	57.70 11.77	26.80 6.85	17.20 5.17	5.38 2.29	3.35 3.38	-33 +13
Hexamethylene Glycol + HE + n-C <sub>8</sub> Acid	0.983 0.920	64.20 14.40	29.53 8.40	19.80 6.26	6.14 2.62	3.16 3.33	-19 + 8
Methylhexamethylene Glycol + HE + n-C <sub>8</sub> Acid	0.995 0.916	87.30 15.40	40.20 8.88	25.30 6.53	7.23 2.71	3.23 3.31	-60 -29
Dimethylolpropane + HE + n-C <sub>8</sub> Acid	0.982 0.920	64.00 14.50	27.90 8.10	17.80 5.87	5.30 2.36	3.46 3.62	
Trimethylolmethane + HE + n-C <sub>8</sub> Acid	1.011 0.944	126 36.20	81.25 17.75	47.07 11.96	10.75 3.86	3.30 3.58	-51 - 8
Pentaerythritol + HE + n-C <sub>8</sub> Acid	1.021 0.959	482 50.79	177.7 23.80	101.1 15.69	19.50 4.73	3.04 3.50	-45 + 7

Table 16

Increasing Molecular Size by Ethoxylation of the Alcohol Employed: 1-C <sub>9</sub> Alcohol by "Oxo" Process on Diisobutylene	Spec. Gr. 20°C	Viscosity in cs., °C				m 20:99	Pour Point, °C
		Viscosity in cs., °C					
		20	38	50	99		
1-C <sub>9</sub> Alcohol + 0 Mole C <sub>2</sub> H <sub>4</sub> O + Adipic Acid	0.918	24.00	12.70	8.70	3.21	3.43	<-72
" + 1 " " " "	0.948	37.60	18.30	12.0	4.30	3.38	-65
" + 2 " " " "	0.976	59.00	27.40	18.30	5.74	3.26	-58
" + 4 " " " "	1.002	92.80	40.90	27.60	7.72	3.13	-52
" + 6 " " " "	1.021	124.60	54.10	34.80	10.00	2.97	-38
" + 0 " " " " Methyladipic Acid	0.916	28.20	14.60	10.00	3.52	3.49	-70
" + 1 " " " " "	0.950	46.00	21.90	14.70	4.73	3.40	-60
" + 2 " " " " "	0.974	66.10	29.07	19.50	6.16	3.24	-55
" + 4 " " " " "	0.998	98.00	42.30	27.10	8.31	3.06	-50
" + 6 " " " " "	1.038	180.00	75.20	47.01	12.50	2.92	-16
Leuna Alcohol 180/250 + 2 " " Adipic Acid	0.972	53.90	24.60	15.70	4.96	3.46	-59
" " " " " " Methyladipic Acid	0.980	78.50	32.80	21.40	6.25	3.38	-54
" " " " " " Sebacic Acid	0.969	119.20	50.60	31.50	8.96	3.10	-55

FIGURE 17



FRICTION TESTING MACHINE

I. G.

1941

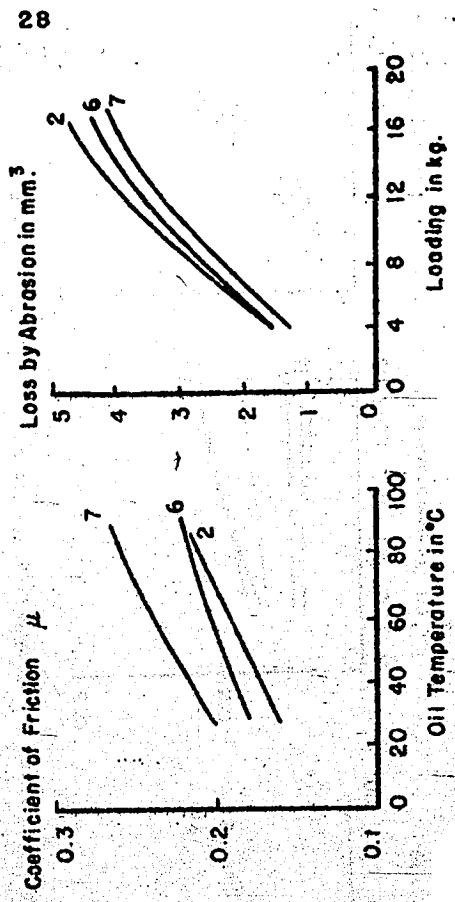
**WEAR EXPERIMENTS**

**Figure 19 - EXPERIMENTS ON**

**THE CHAIN MACHINE.**

Hard Metal Disk against Steel;  
Length of Experiment, 10 min.;  
Oil Temperature, 20°C

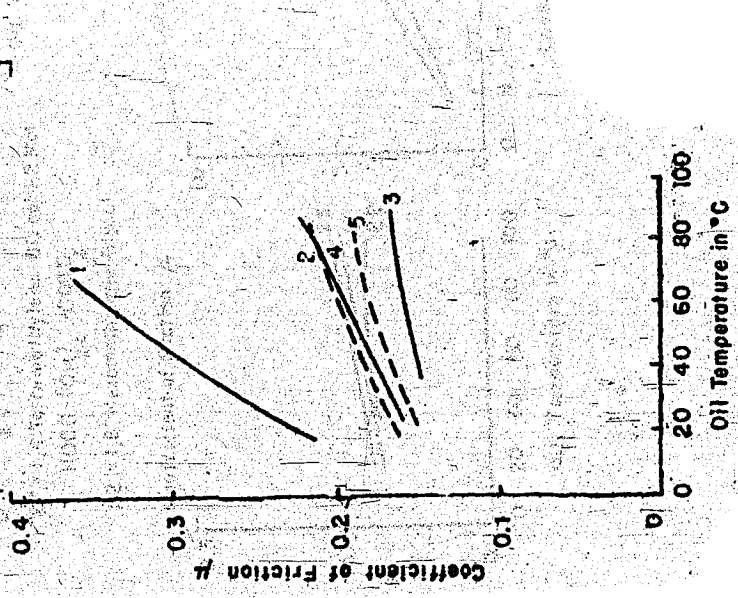
- 2 = Adipic Acid + n-C<sub>8</sub>-Alcohol (350)
- 6 = " + i-C<sub>8</sub> "
- 7 = Methyladipic Acid + i-C<sub>8</sub>-Alcohol (363)



**Figure 18 - EXPERIMENTS ON**

**THE CHAIN MACHINE.**

- 1 = Adipic Acid + n-Butanol (2.3)
- 2 = " + n-Octanol (1.51)
- 3 = " + n-Dodecanol 2.06
- 4 = β-Methyladipic Acid + n-Octanol 1.55
- 5 = β- " + n-Dodecanol 2.07



**WEAR EXPERIMENTS**

**Figure 21-EXPERIMENTS ON THE CHAIN MACHINE.**

Hard Metal Disk against Steel  
Length of Experiment, 10 Min.  
Oil Temperature, 20°C.

25 = Trimethylolmethane + Lauro Carboxylic Acid.

11 = Trimethylolmethane + 1-C<sub>6</sub> Acid.

12 = Trimethylolmethane + Top Cut Fatty Acid C<sub>7</sub>-C<sub>9</sub>

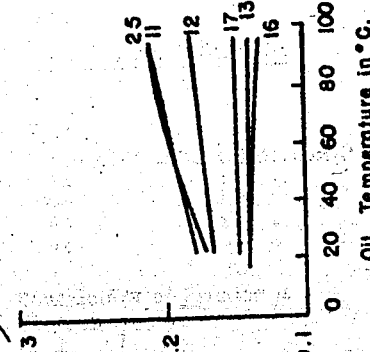
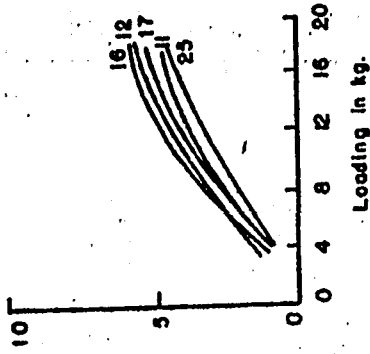
13 = Trimethylolmethane + 3 Mol 1-C<sub>13</sub> - Acid

17 = " " + 2 "

16 = Pentaerythritol + 4 "

Coefficient of Friction  $\mu$

Loss by Abrasion in mm<sup>3</sup>



**WEAR EXPERIMENTS**

**Figure 20- EXPERIMENTS ON THE CHAIN MACHINE.**

23 = Dimethylolpropane + 2 Mol HOOC -(CH<sub>2</sub>)<sub>4</sub> - COOC<sub>6</sub>

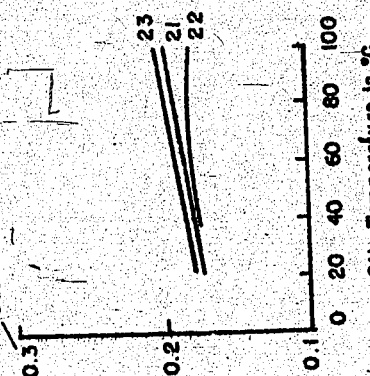
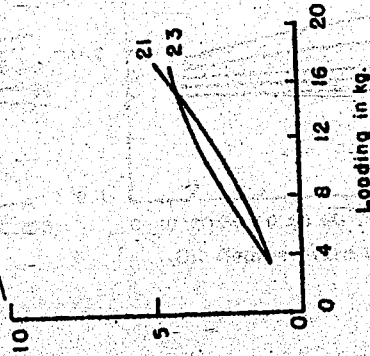
27 = 1,4 Tetramethylene Glycol + 2 Mol HOOC -(CH<sub>2</sub>)<sub>4</sub> - COOC<sub>6</sub>

22 = 1,6, Hexamethylene Glycol "

Hard Metal Disk against Steel  
Length of Experiment, 10 Min.  
Oil Temperature in 20°C.

Coefficient of Friction  $\mu$

Loss by Abrasion in mm<sup>3</sup>



**Figure 22**  
**EXPERIMENTS ON THE CHAIN MACHINE.**

$iC_4-(OCH_2-CH_2)_x + \text{Methyladipic Acid}$		$iC_9 \text{ Alcohol} + 0 \text{ Mol } C_2H_4O + \text{Adipic Acid}$	
33: X = 0		42: "	+ 1 " " "
34: X = 1		43: "	+ 2 " " "
35: X = 2		44: "	+ 4 " " "
36: X = 4		45: "	+ 6 " " "
37: X = 6		46: "	" " " "

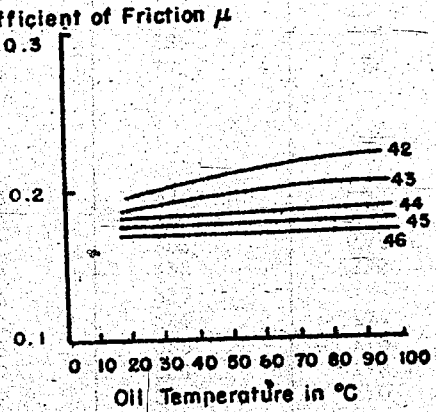
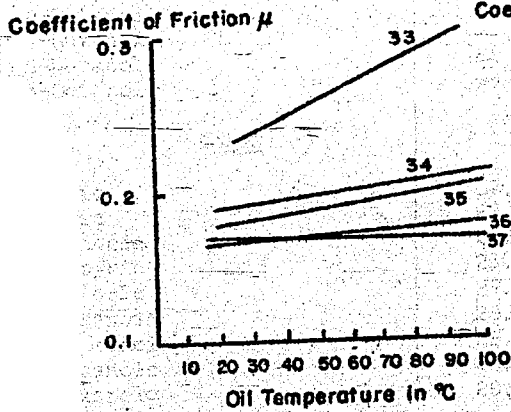


Table 23 Energies of Adhesion for Various Substances  
against Mercury (at 20°C) according to Measurements of  
K. L. Wolff and Coworkers, Halle

Substance	Surface Tension (dynes/cm.)	Interfacial Tension (dynes/cm.)	Energy of Adhesion (ergs/cm. <sup>2</sup> )
<u>Hydrocarbons</u>			
Hexane	19.5	—	120
Cyclohexane	24.7	377	120
Benzene	28.6	366	—
<u>Alcohols</u>			
Methanol	22.5	384	119
Ethanol	22.4	—	—
n-Propanol	23.7	373	125
i-Propanol	23.7	384	117
n-Butanol	24.8	377	—
i-Butanol	—	384	116
n-Hexanol	26.4	372	154
n-Octanol	27	367	—
<u>Acids</u>			
Formic	37.4	393	—
Acetic	27.4	334	174
Propionic	26.5	333	174
n-Butyric	26.6	335	172
n-Valeric	27.4	355	174
n-Hexanoic	28.1	334	174
n-Heptanoic	28.3	335	175
n-Octanoic	28.7	334	175
n-Hexanoic	29.9	332	170
<u>Esters</u>			
Methylacetate	24.9	—	117
Ethyl-	23.0	—	120
n-Propyl-	24.3	—	124
i-Propyl	23.1	369	134
n-Butyl	24.5	374	131
sec-Butyl	23.5	354	150
i-Butyl	22.8	355	140
n-Amyl	25.5	365	141
i-Amyl	24.8	345	—
n-Hexyl	26.3	365	141
n-Heptyl	27.1	357	150
n-Decyl	28.7	343	166
n-Dodecyl	29.1	341	160



Table 24 Differences in Energy of Adhesion against Aqueous and Metallic Surfaces according to Measurements of K. L. Wolff, Halle

Substance	Interfacial Tension (dynes/cm.) against		Energy of Adhesion H (ergs/cm. <sup>2</sup> ) against	
	Water	Mercury	Water	Mercury
Hexane	31.25	380	40.0	120
Benzene	35.05	366	66.6	143
CCl <sub>4</sub>	43.26	358	56.1	149
C <sub>6</sub> H <sub>5</sub> Cl	37.41	350	58.5	163
CS <sub>2</sub>	48.36	341	55.8	170
Mercaptan	26.12	340	68.5	160
Octanol	8.52	367	90.8	140
Heptanoic Acid	6.96	335	94.6	173
Ester	ca.25	ca.350	ca.75	ca.150

Table 25. Rupture Resistance and Adhesive Resistance  
according to Calculations of Prof. Wolff at Halle

Substance	Rupture Resistance (kg./cm. <sup>2</sup> )	Adhesive Resistance (kg./cm. <sup>2</sup> )
Cyclohexane	4900	12500
Benzene	5600	14300
CCl <sub>4</sub>	5600	15000
Ethanol	4500	12000
Propanol	4700	12500
Butanol	5000	12800
Hexanol	5300	13400
Propionic Acid	5300	17400
Butyric Acid	5300	17200
Hexanoic Acid	5600	17400
Heptanoic Acid	5700	17400
Water	14400	16700
Mercury	96000	96000
Brass	5000	
Iron	4000-7000	

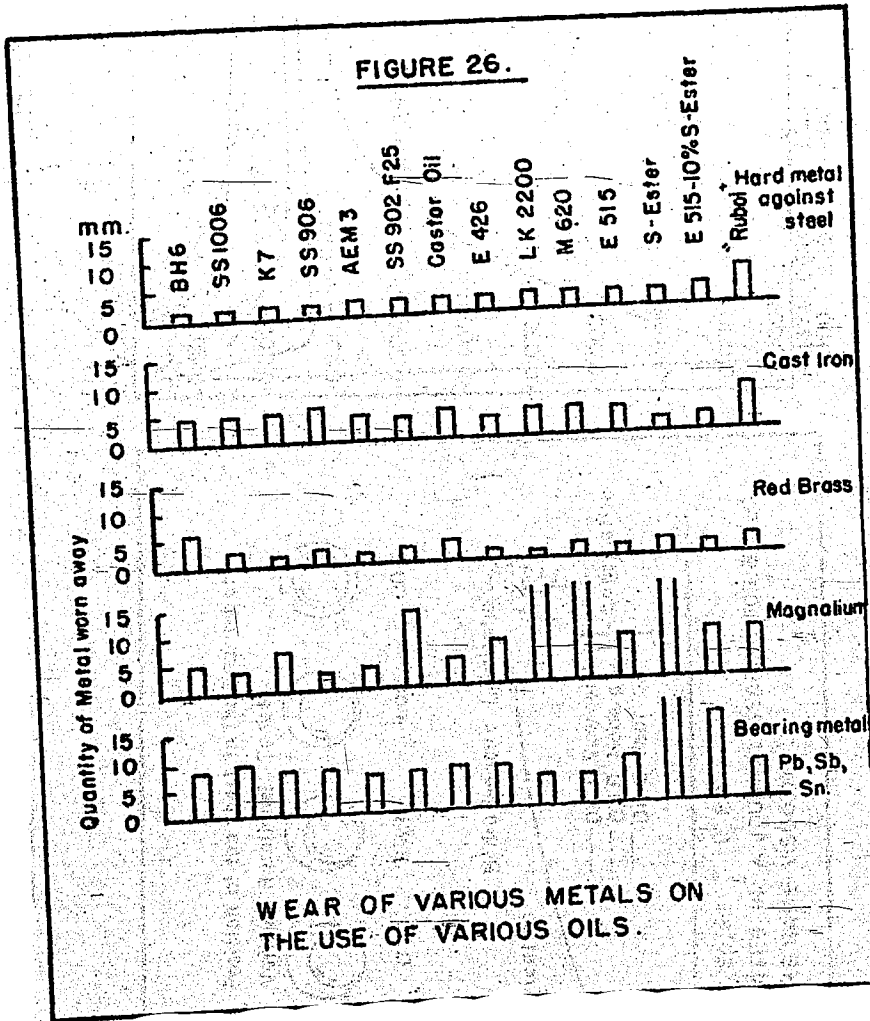
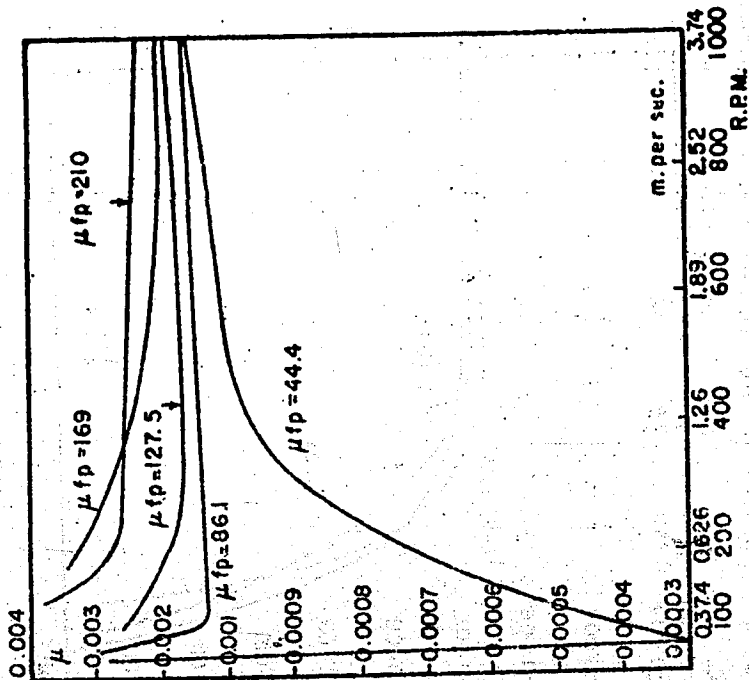


Figure 28



Babbitt Metal: 74 Pb, 14.9 Sb, 6.9 Sn, 2.0 Cd, 1.0 Cu, 1.3 Ni  
 Clearance 0.25 mm, Oil Pressure 3.5 at, Oil Temperature 30°C  
 Oil BC 8, Coefficient of Friction  $\mu$ , Temp. in Oil Film.

Figure 27

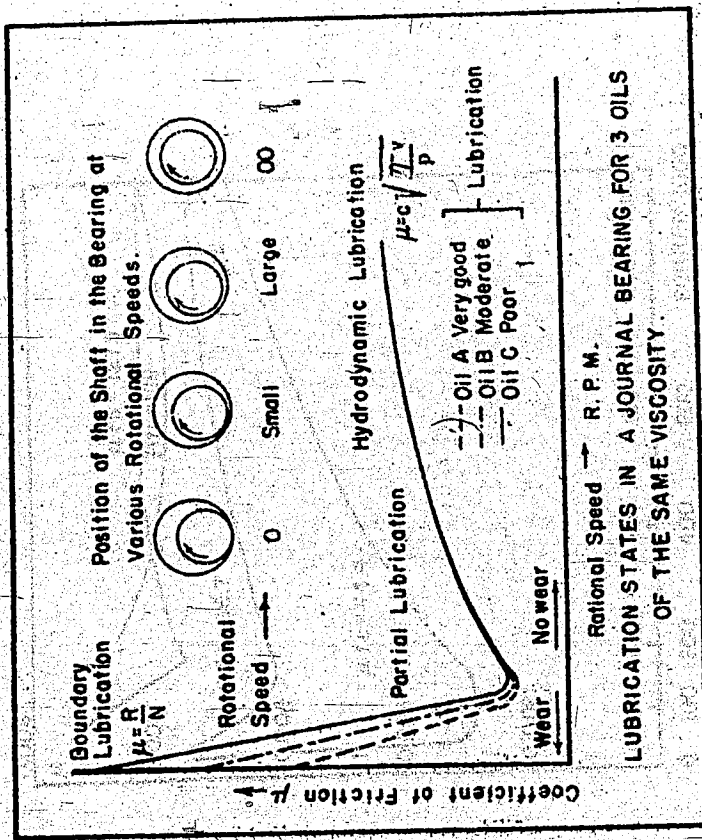
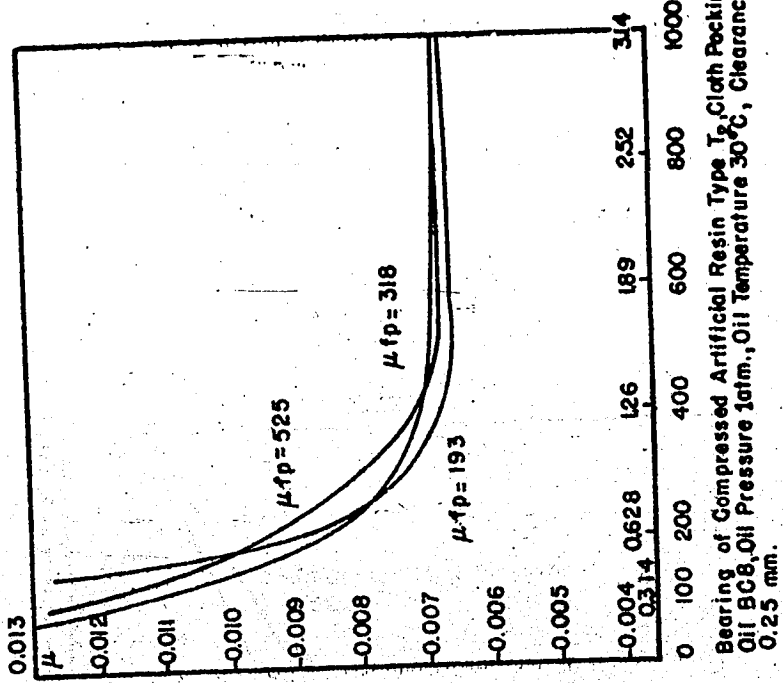
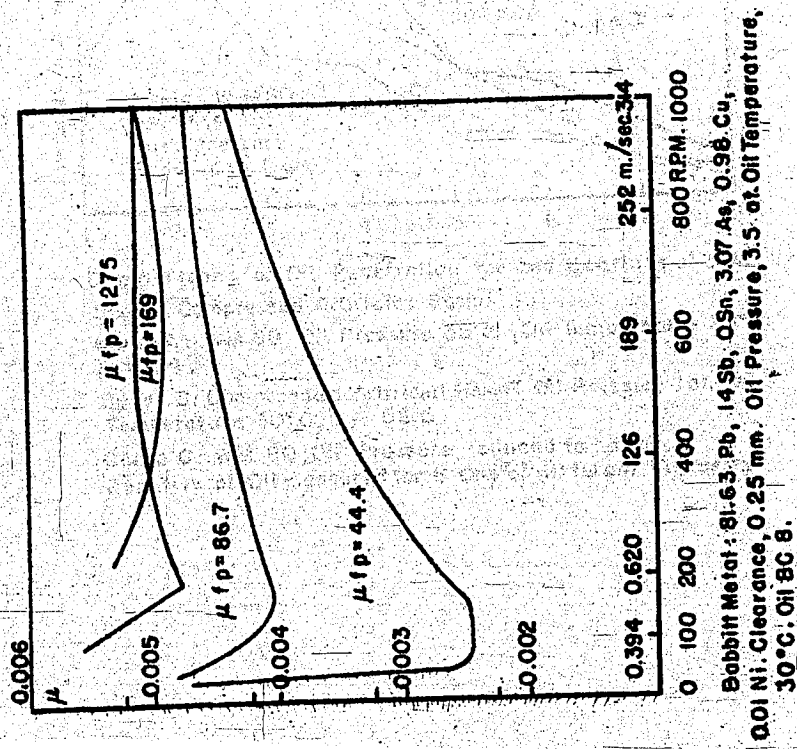


Figure 30.



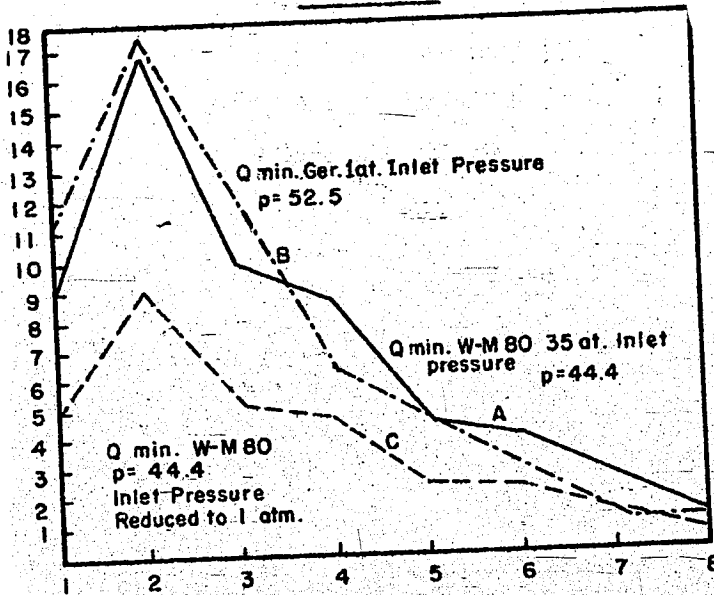
36

Figure 29.



Babbitt Metal: 81.63 Pb, 14.5b, 0.5Sn, 3.07 As, 0.98 Cu,  
 0.01 Ni. Clearance, 0.25 mm. Oil Pressure, 3.5 at. Oil Temperature,  
 30°C. Oil BG 8.

FIGURE 31



Comparisons of Oil Penetration for two Bearings of W-M 80 and Compressed Artificial Resin.  
 Curve A: W-M 80 Oil Pressure 35 at., Oil Temperature 30°C, p = 44.4  
 Curve B: Compressed Artificial Resin. Oil Pressure 1 at., Oil Temperature 30°C, p = 52.5  
 Curve C: W-M 80, Oil Pressure reduced to 1 atm.,  
 Quantity of Oil measured for B Oils of different Viscosity.

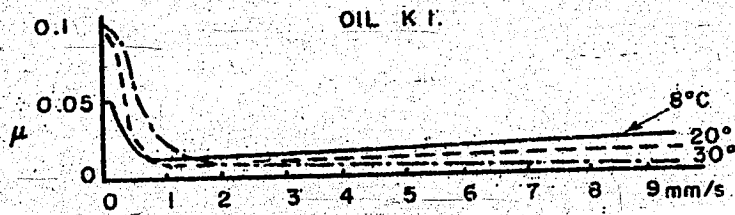
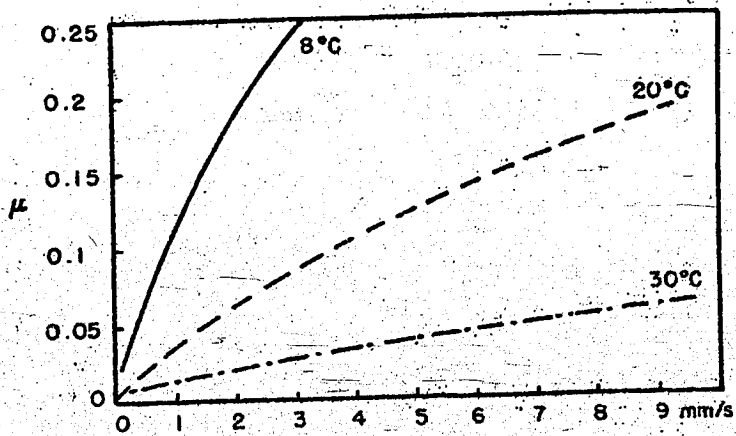
Figure 32 Illegible

Figure 33 Missing

Figure 34 Illegible

Figure 35 Illegible

FIGURE 36.



OIL K2.



Table 37    Illegible

Table 38    Illegible

Table 39 Machine Gun Oils

No.	Type of Oil	Pour Point Below	Viscosity in cs., °C				η	V.P.	50 Shots per Sec.		Length of Firing	Cold Start at
			-55	+28	+38	+99			Begin-ning	End		
440	H.G. - Oil	-55	--	35.2	16.4	3.47	3.406	1.763	2.50	2.51	good after 3000	good to -25°
445	Adipic - S + LA 140/200	-78	4020	13.7	7.58	2.33	3.074	1.136			good after 3000	--
463	K455 + 2% S as C5H11-0-CS-S-S-S-CS-0-C5H11	-78	10720	14.1	7.82	2.28	3.215	1.282	2.55	2.50	good after 3000	--
465	K455 + 5% S	-78	11000	14.3	7.80	2.29	3.221	1.424	2.50	2.52	good after 3000	--
469	K4-011 + 5% S	-78	2765	12.0	6.96	2.17	3.129	1.145	2.50	2.50	frozen after 2500	--
495	K4-011 + 5% S	-78	3185	11.9	7.07	2.16	3.181	1.204	2.50	2.50	good after 3000	good to -25°
494	K4-011 + K405 1:1 + 2.5% S	-78	5290	13.0	7.40	2.22	3.186	1.235	2.52	2.50	good after 3000	good to -25°

Table 40 German Axle Oils

	Winter Oil 2/191 XXX	Winter Oil 2/1 XXX	Winter Oil 2/-- XXX	Winter Oil 2/194 XXX	Winter Oil 2/61 XXX
Asphalt	0.08	0.7	1.0	0.02	0.5
Resins $\text{CHCl}_3$	8.7	11.8	11.3	15.5	15.5
Carbon Pyridine	3.4	3.8	1.8	1.6	1.6
$\text{H}_2\text{SO}_4$ - Soluble 6 x 2 to 3 cc.	10.2	16.7	—	18.0	11.7
Acetone - Insoluble 20°	3.3	6.9	10.4	4.6	9.8
Wax	2.0	2.2	2.9	4.5	3.9
HC Oil	64.6	58.6	51.4	57.9	58.7

Table 41

Type of Oil	Pour Point, °C	Viscosity, °					V. I.
		-50	-20	+38	+50	+99	
1) 2/166	-40	16380	2583	10.97	6.00	1.715	75
2) 2/191	-34	37100	1710	8.61	4.81	1.600	73
3) 2/1	-43	7076	1511	8.24	4.78	1.630	98
4) 2/61	-44	5359	1248	8.27	4.85	1.643	98
5) 2/194	-38		1482	8.21	4.83	1.658	104
Mixtures							
6) 2/166 + 2/191	-35	24630	2192				
7) 2/1 + 2/61 + 2/194	-35	6574	1155				
8) 2/61 + 2/194	-40	8800	1270				
9) 2/1 + 2/194	-34	7273	1225				
10) 2/1 + 2/61	-42	6093	1322				
11) Mixture 1 - 5	-35	9393	1595	9.41	5.30	1.657	81
12) Ester 436	-74	520	203	1.75	1.53	1.17	169
13) M 1 - 5 + 12% Ester	-40	3235	729	6.75	4.03	1.543	95
14) Mixture 7 + 6% Ester	-41	3390	931	7.11	4.23	1.584	101
15) Mixture 7 + 12% Ester	-44	2285	660	6.07	3.74	1.521	102

Table 42 Capillary Flow of Natural Axle Oils

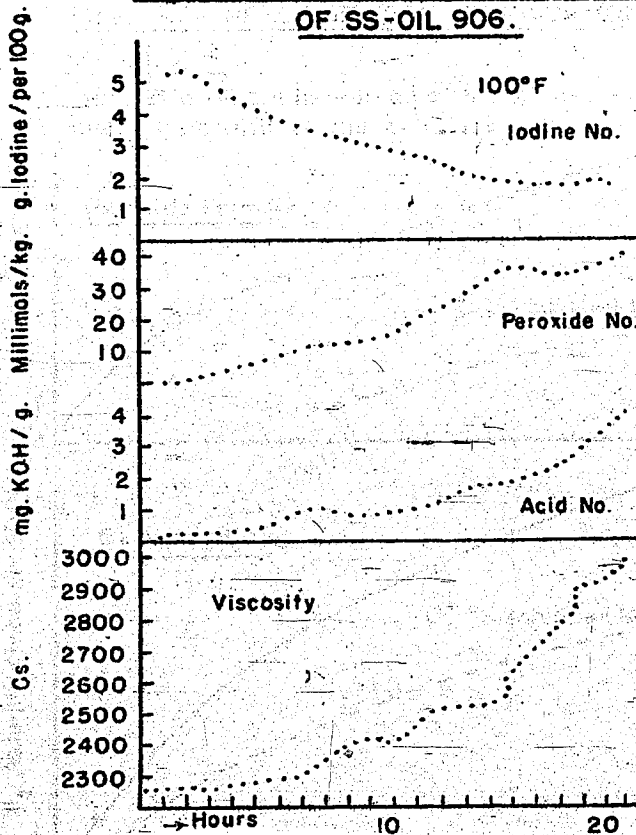
Type of Oil	At +50°			At +20°			At -10°		
	1 week	6 weeks	Total Quantity	1 week	6 weeks	Total Quantity	1 week	6 weeks	Total Quantity
1	379	265	1912	128	120	760	0.1	4.3	25
2	299	101	1050	20	0.6	26	0	0.5	0.9
3	389	325	2125	126	119	756	3.0	9	52
4	355	181	1517	90	81	529	0	1.3	4.5
5	409	349	2332	122	117	741	0.4	4.4	23
Mixture 1 - 5	378	243	1807	81	22	245	0.1	2	12
Mixture 1 - 5 + 12% Ester	511	359	2525	121	52	461	0.8	3.4	22
Mixture 1 - 5 + 10% Gas Oil	433	240	1980	152	141	901	11	18	114

Table 43    Illegible

Table 44    Illegible

Table 45    Illegible

**Figure 46 - DETERIORATION ON OXIDATION  
OF SS-OIL 906.**



**Figure 47 - DETERIORATION ON OXIDATION OF  
SS-OIL-906.**

Test : 20g. Oil are irradiated with U.V. light in  $O_2$   
Atmosphere with violent agitation.

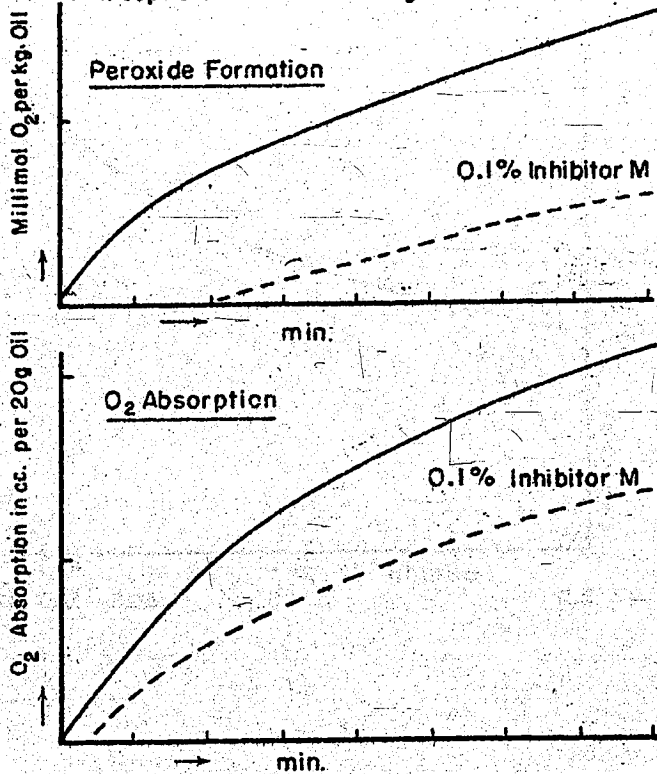




Figure 48DETERIORATION ON OXIDATION OF S.S. OIL 906

Dependence of Viscosity Increase on Inhibitor Content.

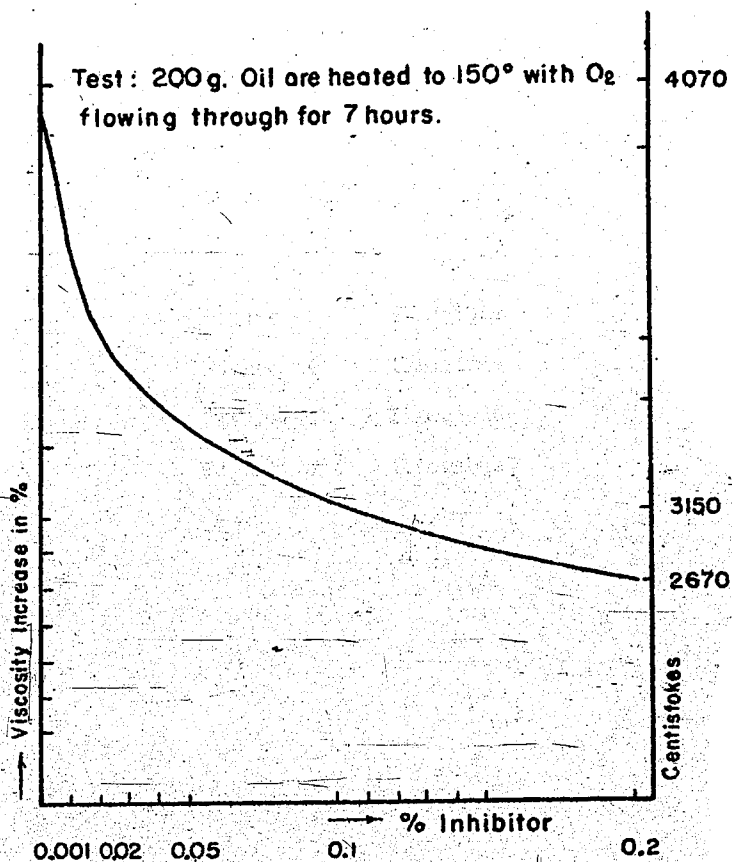


Figure 49      Illegible

Figure 50      Illegible

Figure 51      Illegible

Figure 52      Illegible

Table 53

No.	Type of Oil	Length of Run Improvement over Stanave
1	Lubricating Oil Distillate from Nienhagen Oil refined with $AlCl_3$ + SS 1100 1:1	23%
2	Copolymer of the above Nienhagen Oil and Cracked Wax Product 1:1	48%
3	Nienhagen - Lubricating Oil Distillate Treated with Propane then Refined with $AlCl_3$ and Mixed with SS 1100 1:1	25%
4	Nienhagen - Lubricating Oil Distillate Treated with Propane then Copolymerized with Cracked Wax Product 1:1	100%

Figure 54

