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LUBRICITY CHARACTERISTICS OF CORROSION PREVENTIVE OILS

TECHNICAL REPORT

By

Chas. J. Quilty

December 1966

U. S. ARMY WEAPONS COMMAND

ROCK ISLAND ARSENAL

RESEARCH & ENGINEERING DIVISION

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LUBRICITY CHARACTERISTICS OF CORROSION PREVENTIVE OILS

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DA #1CO24401A109

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ABSTRACT

In this study, seventeen qualified preservative oils were investigated to establish their lubricity properties. The oils were tested in a Shell Four-Ball Wear Tester at selected loads and the wear scars measured. The viscosity and acidity of each oil were determined before and after wear test. Adhesive wear particles formed during wear tests were examined microscopically and their size shown to be an indication of the lubricating ability of the oil. Results indicate that these oils have considerable room for improvement in their lubricating ability.

A new method, using thermometric titrimetry, was developed for determining acidity in new and used corrosion preventive and lubricating oils. The total acid numbers obtained by colorimetric, potentiometric, and thermometric methods were compared.

FOREWORD

The work reported here was conducted under DA Project No. 1CO24401A109, AMS Code 5025.11.803, "Corrosion Preventives and Specialty Compounds." The work unit title was "Lubricity Properties of Corrosion Preventives." The work was performed for the purpose of determining the lubricating ability of currently used corrosion preventive oils.

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PROBLEM

To determine the lubricity characteristics of qualified preservative lubricating oils and to determine the effect of wear on selected properties of the oils.

BACKGROUND

In the past the major items of technical interest for corrosion preventive lubricating oils have been their corrosion preventive ability and their physical properties. Lubricity characteristics were of secondary importance; it being assumed that a good quality mineral oil should perform satisfactorily in this regard. Increasing severity of applications for these oils requires that good lubricity properties often be present.

Prevention of wear by an oil requires the presence of an additive, either a polar compound or an extreme pressure (EP) agent which reacts to form a solid film lubricant. Corrosion preventive oils generally contain other additives such as corrosion and oxidation inhibitors. Because of the possibility that these other additives might interfere with the activity of the lubricity additive, or vice versa, it is necessary to test the oils by established methods.

The logical initiation of this investigation was to determine the wear characteristics of currently qualified oils so that the data accumulated might serve as a starting point for establishing test methods, requirements, and the possible need for improvement in the wear properties of these oils.

APPROACH

Qualified samples of VV-L-800[1], MIL-L-3150A[2] MIL-L-14107B[3], and MIL-L-21260 (Grades 1, 2, and 3)[4] preservative lubricating oils were tested according to the following procedure:

1. Duplicate tests were run in the Shell Four-Ball Wear Tester at loads of 1 kg., 10 kg., and 40 kg. The unit was operated at 1200 RPM and 75°C for 1 hour using composition 52100 steel balls and 10 ± 1 ml of the test oil.

2. After testing at 1 kg. and 40 kg. loads, the used oil was filtered through a filter paper of suitable porosity. The dried filter paper was then examined microscopically to determine the nature and quantity of the wear particles.

3. The oil filtrate from the Four-Ball Test was then titrated potentiometrically[5] and thermometrically[6], and the viscosity at 100°F determined. The acidity and viscosity of the original oils were also determined for comparison purposes.

THERMOMETRIC TITRIMETRY

The determination of acidity in corrosion preventives and lubricating oils by thermometric titrimetry represents a new method of analysis developed during this investigation. This method of titration consists of the detection and measurement of the enthalpy change (ΔH) of a solution as titrant is added to it, under as nearly adiabatic conditions as possible. A significant characteristic of thermometric titrations is their applicability to situations where the free energy change is small, while the heat of neutralization is appreciable. The alkaline titrations of corrosion preventive oils present an almost ideal situation of this type. For this reason, thermometric titrimetry offers a simple, rapid method of analysis for a considerable number of petroleum base materials.

A photograph of the Titra-Thermo-Mat[7] is given in Figure 1. It consists essentially of: (a) a Menisco-matic buret, (b) an adiabatic titration tower, (c) a thermistor-bridge assembly, and (d) a high impedance recording D.C. potentiometer. Operation of this instrument is entirely automatic with the off-balance potential of the thermistor bridge - time presentation being recorded on the potentiometer. The Menisco-matic buret has a constant flow speed of 600 μl min^{-1} so that the recorded time is proportional to the volume delivered. An electrical calibration may be performed so that the unbalance - potential of the thermistor-bridge may be converted to either temperature or calories.

To perform the electrical calibration, a simulated exothermic titration is carried out using the instrument heater and 20 ml. of water. The heater is a 4-ohm manganin wire and is energized by a 2.6 volt (max.) nickel cadmium battery. By measuring the voltage applied to the heater and the length of time the heat is applied, the caloric output may be obtained using equation [1]. By varying the time the heater is energized, a series of points indicating

$$\frac{(\text{voltage})^2}{\text{resistance}} \times \frac{\text{time (sec)}}{4.2} = \text{calories} \qquad [1]$$

calories versus recorder output may be obtained. An electrical calibration curve for the Titra-Thermo-Mat is shown in Figure 2.

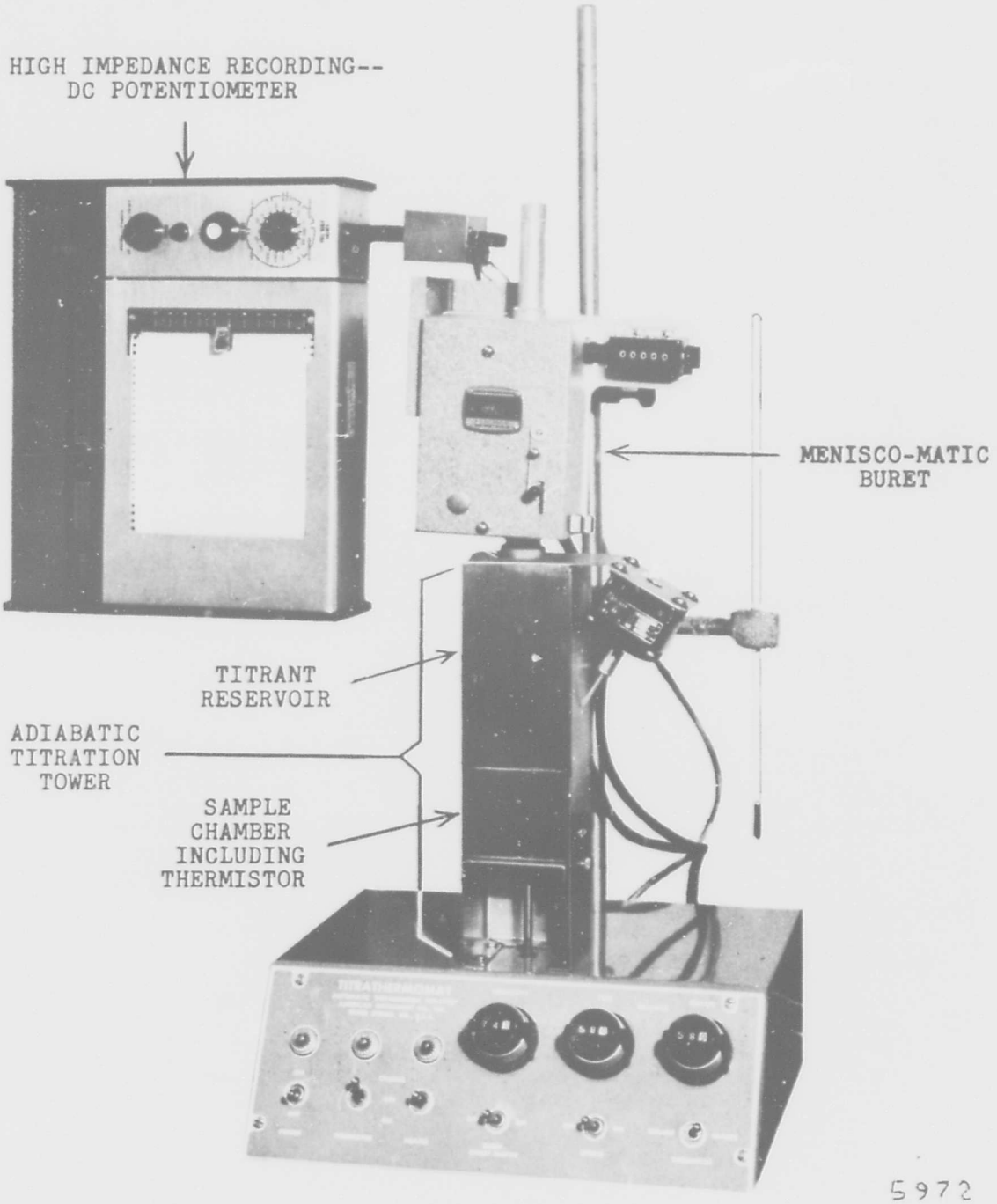


FIGURE 1 THERMOMETRIC TITRATION APPARATUS

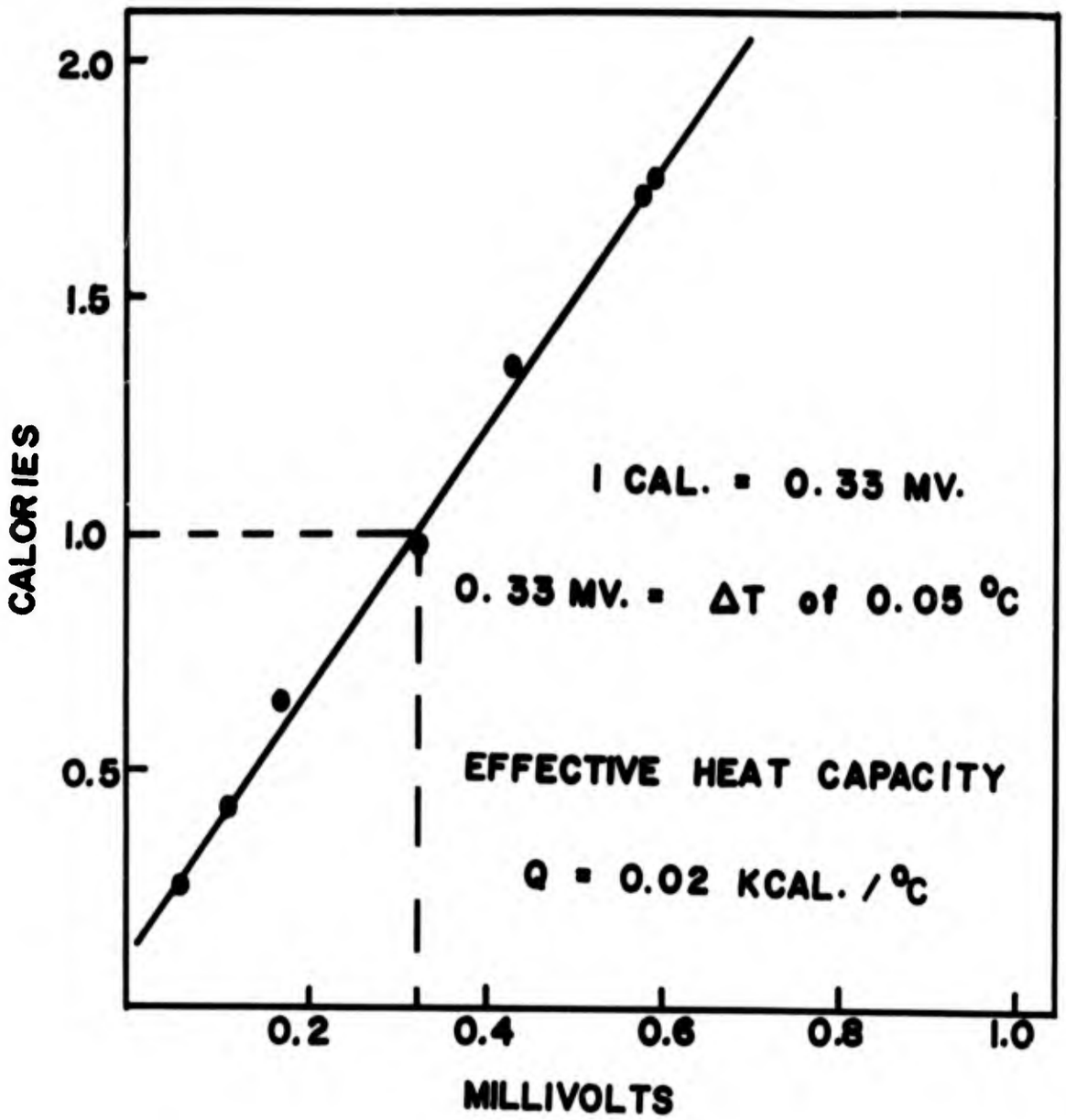


FIGURE 2 ELECTRICAL CALIBRATION CURVE FOR THE TITRA-THERMO-MAT

To perform an actual titration of a corrosion preventive oil the following procedure is used:

1. A sample of oil, preferably 0.5 - 1.0 gm, is weighed accurately to ± 0.1 mg in a clean 30 ml tall-form beaker.

2. The sample is then dissolved in 20 ml of isopropyl alcohol and placed in the titration tower.

3. Using the thermistor selector switch, the temperature of the titrant and titrate are compared. The heater is then used to bring the solutions to within 0.2°C of each other.

4. The titration is then performed using a 0.1 or 0.2 $\underline{N}$ solution of KOH in isopropyl alcohol as the titrant. This solution is prepared as in ASTM D664-58[5] and standardized by titration of a weighed quantity of potassium acid phthalate. The solution should be kept in a chemically resistant bottle.

5. Interpret the resultant titration curve as shown in Figure 3 and calculate the total acid number from equation [2].

$$TAN = 56.1 \times Ml_{KOH} \times \underline{N}_{KOH/W} \qquad [2]$$

where: TAN = total acid number in mg KOH/gm
Ml_{KOH} = number of milliliters of KOH required to reach the end point
$\underline{N}_{KOH}$ = normality of the KOH solution
and W = weight of the sample in grams

If the heat of neutralization (ΔH) is desired, the electrical calibration is used to convert the recorder output to temperature. Equation [3] may then be used to calculate ΔH. Values obtained in this way are accurate to within 5-10%.

$$\Delta H = \Delta T \times Q/N_m \qquad [3]$$

where: ΔH = heat of neutralization in Kcal $mole^{-1}$
ΔT = change in temperature in °C
Q = effective heat capacity (obtained from calibration) in Kcal/°C
and N_m = number of moles of KOH required to neutralize the sample

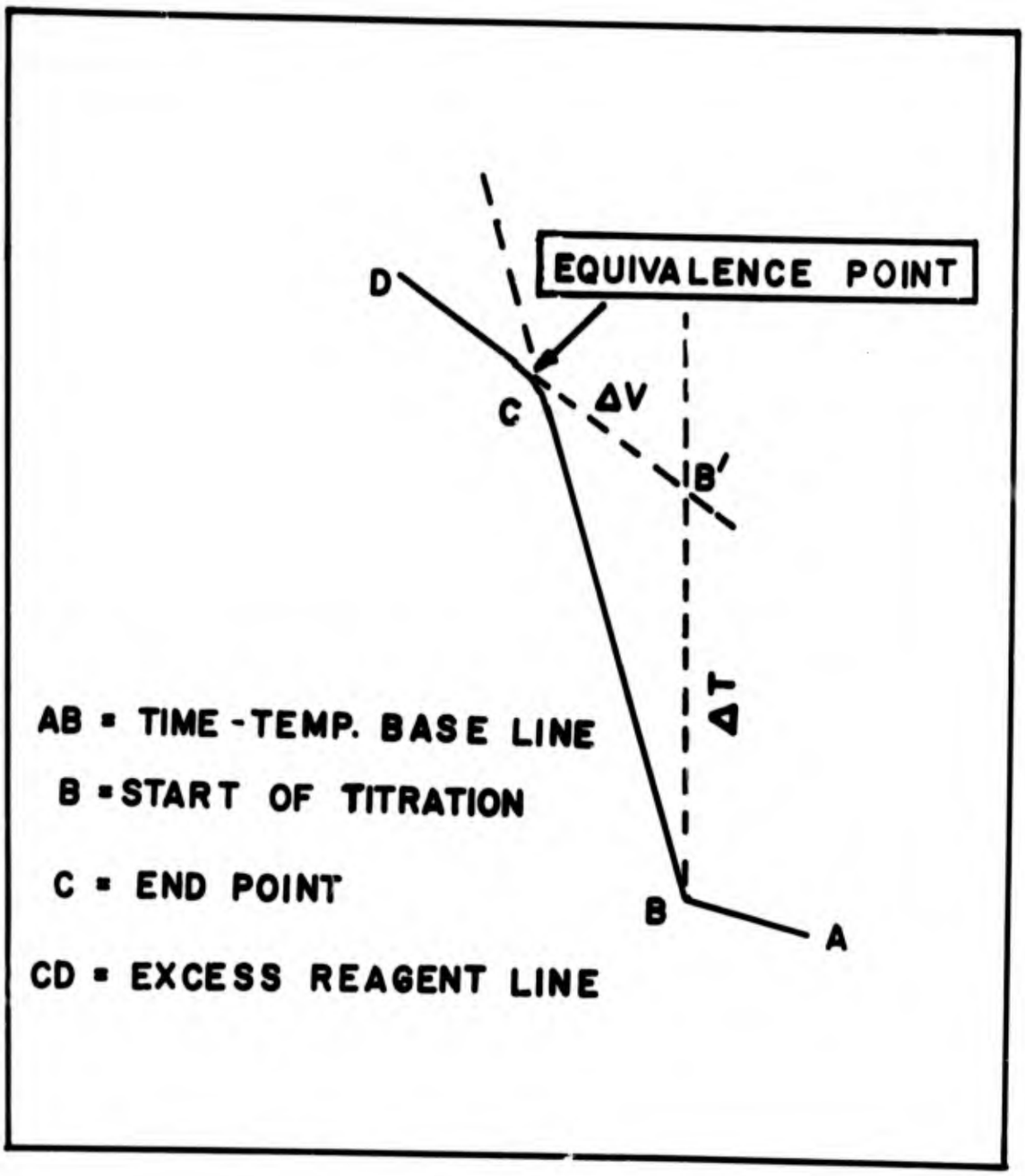


FIGURE 3 TYPICAL THERMOMETRIC TITRATION CURVE OF A CORROSION PREVENTIVE OIL

RESULTS AND DISCUSSION

For this investigation, seventeen oils qualified under federal specification VV-L-800 and military specifications MIL-L-3150A, MIL-L-14107B, and MIL-L-21260 (Grades 1, 2, and 3) were tested. A summation of the results obtained on these oils is presented in Table I.

A plot showing the effect of load upon the lubricity of the oils is given in Figure 4. Curve A shows the performance obtained with MIL-L-14107B oils. This material has a tetra-alkyl silicate ester as a base fluid. The silicate esters are usually non-corrosive to most metals, one reason being that their thermal and hydrolytic decomposition products are not highly acidic as witnessed by the small changes of acidity shown in Table I. Silicate esters themselves do not inhibit corrosion; this must be accomplished by the use of an additive. The boundary lubricating ability of the silicate esters is only fair as illustrated by the steep slope of curve A in Figure 4.

VV-L-800, MIL-L-3150A, and MIL-L-21260 oils (curves B, C, and D respectively in Figure 4) are mineral base oils and give a similar type of curve).

The lubricating ability of the VV-L-800 and MIL-L-3150A oils is relatively good as compared with MIL-L-14107B oils. MIL-L-21260 oils gave very good performance as illustrated by their wear scars and the small slope of the wear curve. Because test conditions were in the boundary lubricating region rather than the hydrodynamic region, the viscosity differences of grades 1, 2, and 3 had no effect on the wear scars obtained.

Curve E of Figure 4 shows the wear curve obtained when a perfect or ideal lubricant is used.

The viscosity changes in the VV-L-800 oils were moderate and were probably caused by thermal and oxidative degradation. Many of the MIL-L-3150A and MIL-L-21260 oils exhibited excessively large viscosity changes. These two types of oil probably contain high-molecular weight polymers as thickeners and dispersants, and the bulk of the large viscosity changes is probably due to the shearing of these polymers during the wear test.

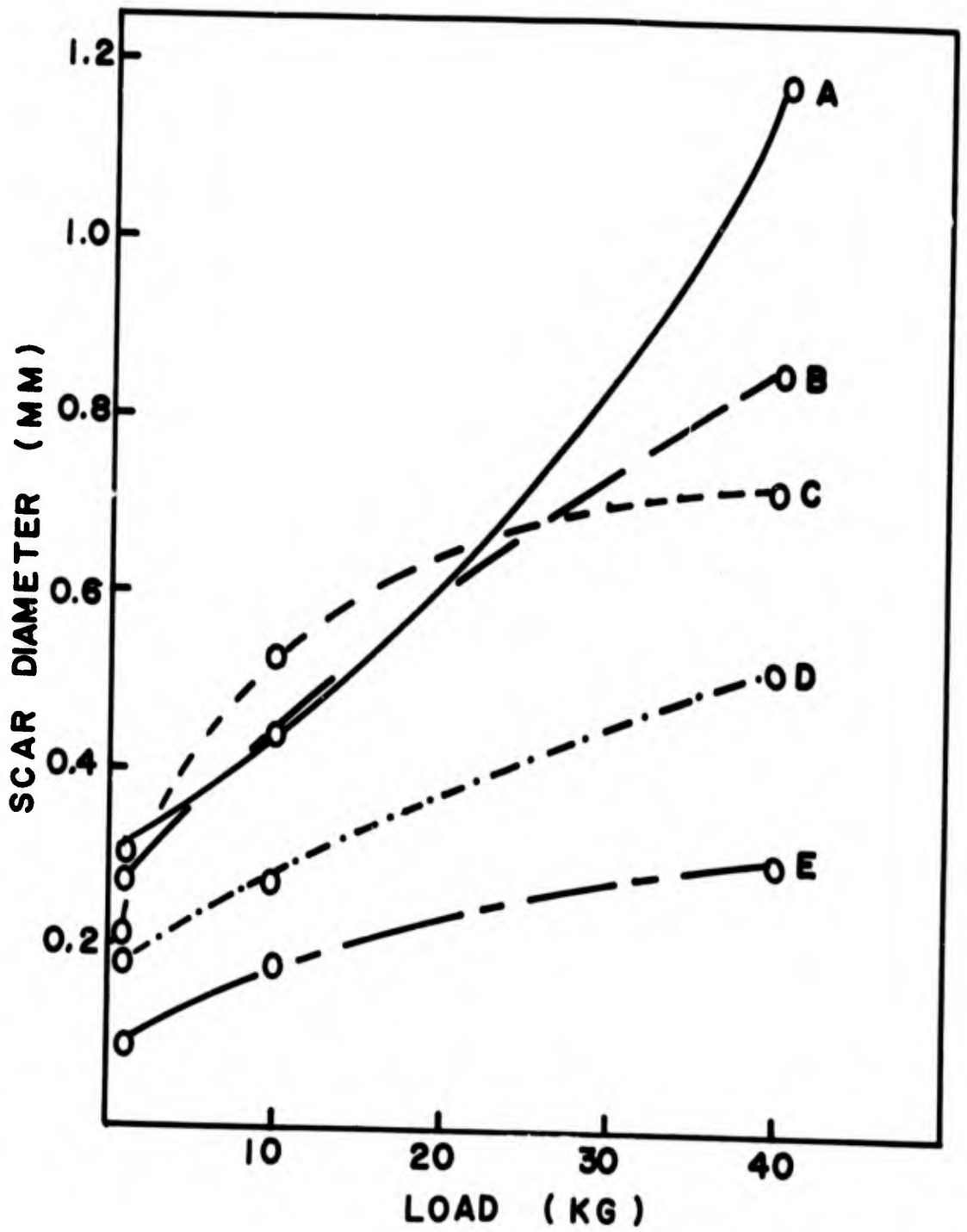
Although many MIL-L-21260 oils showed quite large acidity changes, the greater percentage of the oils tested did not.

TABLE I

WEAR PROPERTIES OF CORROSION PREVENTIVES

Oil	Original Oil TAN[1] (mg KOH/gm)	Original Oil V_k[2] (cs)	1 Kg Load 4-Ball Wear Scar[3] (mm)	1 Kg Load ΔTAN (mg KOH/gm)	1 Kg Load $\%\Delta V_k$	10 Kg Load 4-Ball Wear Scar[3] (mm)	40 Kg Load 4-Ball Wear Scar[3] (mm)	40 Kg Load ΔTAN (mg KOH/gm)	40 Kg Load $\%\Delta V_k$
				VV-L-800 OILS					
A	2.76	12.28	0.28	0.57	-1.4	0.48	0.96	0.69	0.8
B	0.06	13.19	0.26	0.12	-1.8	0.40	0.78	0.62	-1.8
C	1.00	12.11	0.30	0.02	-0.9	0.42	0.74	1.53	-2.5
D	0.15	12.29	0.30	0.19	-1.8	0.48	0.79	0.48	-1.9
				MIL-L-3150A OILS					
E	3.28	121.53	0.22	1.06	0.1	0.56	0.79	0.37	-12.8
F	1.77	120.77	0.20	0.36	-18.5	0.50	0.65	0.47	-17.6
				MIL-L-14107B OILS					
G	2.53	6.48	0.32	0.06	-1.5	0.46	1.20	0.15	-0.8
H	2.31	6.39	0.29	-0.35	-5.5	0.42	1.16	-0.15	-15.6
				MIL-L-21260 OILS					
				GRADE 1					
I	1.63	42.98	0.18	0.76	2.2	0.30	0.54	-0.47	6.0
J	0.66	54.05	0.17	1.85	-21.1	0.26	0.56	0.17	-21.0
K	4.64	39.12	0.20	4.09	-0.8	0.29	0.47	1.54	+2.5
				GRADE 2					
L	1.00	121.83	0.18	1.14	-0.1	0.25	0.55	0.42	3.0
M	0.99	110.37	0.18	1.89	-1.7	0.26	0.58	0.99	-0.6
N	5.46	130.58	0.17	3.21	-4.0	0.26	0.50	1.08	0.5
				GRADE 3					
O	1.89	300.66	0.16	1.22	-5.2	0.26	0.50	-0.02	-7.4
P	1.20	245.02	0.17	1.65	-4.8	0.26	0.58	0.38	-4.7
Q	5.84	298.70	0.17	2.58	-5.5	0.24	0.54	2.28	-5.4

1 Total Acid Number by Potentiometric Titration
2 Kinematic Viscosity at 100°F
3 1200 RPM, 75°C, 1 Hour



A - MIL-L-14107B
B - VV-L-800
C - MIL-L-3150A
D - MIL-L-21260
E - Mean Hertz Diameters

Values are mean scar diameters for the oils tested.

FIGURE 4 EFFECT OF LOAD ON WEAR

Another aspect of this investigation involved a study of the particles formed during wear tests. The formation of an adhesive wear particle on a steel surface requires the existence of a strong bond. For loose particles to occur this bond must be weakened and broken. Chemical conversion of adherent steel particles to Fe_2O_3 fragments which come off loose is one possible mechanism. The other mechanism involves the residual elastic energy in a particle after it has been in a state of severe stress and strain. For the particle to come off loose, the elastic energy must be equal to or greater than the energy of adhesion at the particle - substrate interface.

By a mathematical treatment of the above mechanisms, Rabinowicz[8] has shown that

$$\delta = 60{,}000 \frac{W_{ab}}{p} \qquad [4]$$

where:

δ = diameter of loose wear particles
W_{ab} = work of adhesion
and p = penetration hardness of the metal

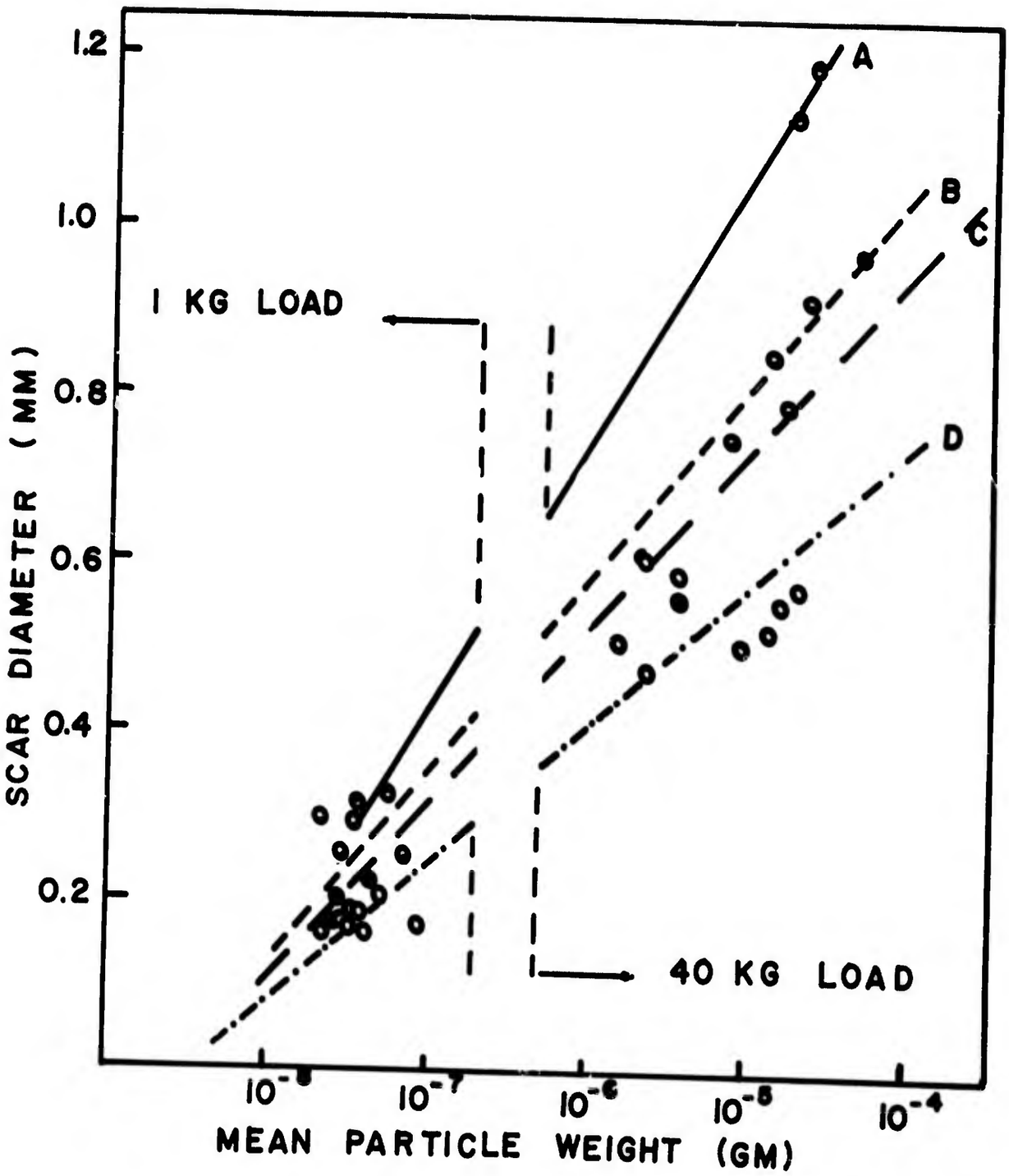
In this study, p was constant so that we may say:

$$\delta \propto W_{ab} \qquad [5]$$

This simple relationship shows that for a given system, the effectiveness of a lubricant can be judged by its ability to reduce W_{ab} and thereby the size of wear particles formed.

In this study a rough estimate was made of particle size by counting all particles exceeding 25μ in size and dividing the weight loss of the steel balls due to wear by the number of particles counted. The slopes of the plots in Figure 5 are proportional to W_{ab} for each lubricant system. It is apparent that a lower value of W_{ab} (smaller slope) gives the most effective lubrication.

Table II gives a comparison of the three methods used for determining the total acid number of the oils. It is evident that no correlation exists between the three methods although the potentiometric and thermometric methods show better correlation than the colorimetric method does with either. Titrations of over forty samples of new and used oils showed that the thermometric procedure developed gave almost twice the precision obtained using the potentiometric method. Heats of neutralization for the oils titrated ranged from - 1 to -29 Kcal/mole.



A - MIL-L-14107B
B - VV-L-800
C - MIL-L-3150A
D - MIL-L-21250

FIGURE 5 EFFECT OF PARTICLES ON WEAR

TABLE II

COMPARISON OF TITRIMETRIC PROCEDURES FOR DETERMINING ACIDITY OF CORROSION PREVENTIVE OILS[a]

Original Oils

Oil	Colorimetric	Potentiometric	Thermometric
A	0.32	2.76	1.36
B	0.26	0.06	-
C	3.82	3.28	3.15
D	0.02	2.53	1.72
E	0.16	1.00	1.08
F	0.09	1.20	4.86
G	0.74	4.64	1.59

Used Oils

H	-	3.33	0.95
I	-	1.02	0.95
J	-	0.34	0.38
K	-	4.34	3.16
L	-	2.59	1.55
M	-	1.16	0.98
N	-	1.42	0.80
O	-	1.87	1.11

[a] All figures are Total Acid No. in mg KOH/gm.

CONCLUSIONS AND RECOMMENDATIONS

Results of this investigation have shown that the lubricity properties of currently qualified samples of preservative oils leave considerable room for improvement. It is suggested that the use of anti-wear and/or extreme-pressure additives might greatly enhance the lubricating ability of these oils.

Thermometric titrimetry is a simple, rapid method for the determination of acidity in corrosion preventive oils. It has wider applicability and equal or superior precision than established methods. It is therefore recommended that the thermometric procedure be used in place of the conventional methods.

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