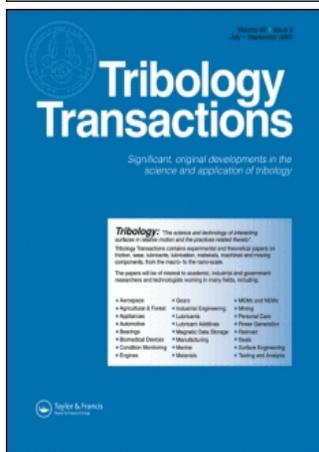


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Surface Chemistry of Chlorinated Hydrocarbon Lubricant Additives—Part I: Extreme-Pressure Tribology[©]

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Chlorinated hydrocarbons are commonly added to a base lubricating fluid when it is used for extreme-pressure (EP) lubrication of ferrous metals. It is demonstrated here that the interfacial temperature in the EP regime varies linearly with the applied load in a pin and v-block testing apparatus and that temperatures in excess of ~1000 K can be attained. Thermally decomposing chlorinated hydrocarbon vapors on iron heated to these temperatures (1) shows that a film consisting of an iron chloride which incorporates small carbon particles (~50 Å) is formed. In this paper, tribological measurements at extreme pressures and the corresponding analyses of the rubbing surfaces and wear particles also indicate that this film, formed from the chlorinated lubricant reacting with these surfaces, is the critical anti-seizure material at less severe EP loads and interfacial temperatures less than ~1000 K.

KEY WORDS

Additive Deposition; Auger Electron Spectroscopy (AES); Barrier Films; Extreme-Pressure Additives; Ferrous Alloys; Iron; Metalworking; Materials Machining; Thermal Degradation; Thermal Effects; X-ray Photoelectron Spectroscopy (XPS)

INTRODUCTION

In an effort to gain a fundamental understanding of tribology "in the extreme" using ferrous metals, the authors have undertaken a detailed investigation of perhaps the chemically simplest, as well as most economical, class of extreme-pressure (EP) additives in common use, those containing chlorine. Well-defined chlorinated hydrocarbons were added to a member of the relatively inert poly- α -olefin group of hydrocarbons. This was chosen because of its similarity to commercial base fluids. The tribological effectiveness

of the model lubricant was determined in the EP regime, i.e., where solid interfacial material containing iron is continually being removed. Experience has shown that chlorinated hydrocarbons appear to be irreplaceable in many very heavy-duty operations, such as severe stainless-steel metalworking, forming brake drums, or fineblanking heavy parts for the auto industry. Thus, for many lubricant manufacturers, this class still represents the greatest tonnage of EP lubricant additive utilized. Recent recycling and various handling improvements have effectively addressed most environmental concerns.

Perhaps the simplest tribological testing technique in common use, the pin and v-block apparatus, was employed together with more fundamental film growth and surface analytical measurements on ferrous metal surfaces using chlorinated hydrocarbons in order to relate EP tribological phenomena to the surface chemistry of the additive (2). In this paper, it is demonstrated that careful use of this apparatus leads to the discovery of a "critical" interfacial temperature defining lubricant failure as well as a mathematical relationship between load and temperature (3). In Part II (1), film growth kinetics are measured using identical chlorinated hydrocarbons on polycrystalline iron foils using a microbalance so that temperature and pressure (concentration) effects could be accurately measured and a mechanism for film growth on iron determined.

EXPERIMENTAL

Pin and V-block Apparatus and Tribological Test Procedure

Figure 1 shows the basic tribological apparatus utilized for all seizure load and wear determinations for various model lubricant combinations discussed below. These consisted of a pure chlorinated hydrocarbon dissolved in a well-characterized, commercially available, 4 cSt poly- α -olefin

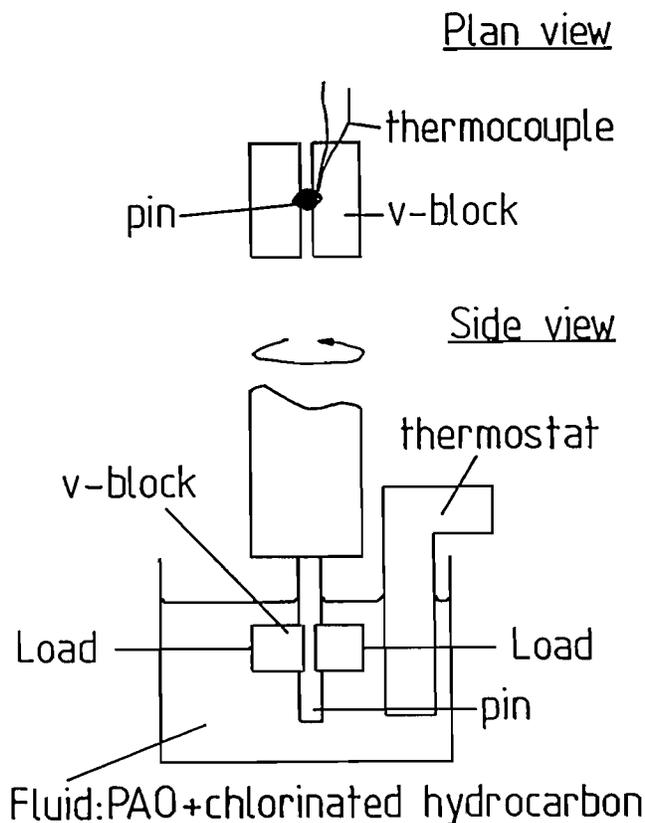


Fig. 1—Schematic diagram of pin and v-block apparatus modified for temperature measurement and control.

(PAO). This diluent is 9-methyl-11-octylheneicosane or the hydrogenated, addition trimer of 1-decene with small concentrations of the dimer, tetramer and pentamer; water and oxygen contents were also found to be at the parts per million and billion levels, respectively (2). Compared to other model hydrocarbon fluids commonly used to mimic commercial mineral oils, this PAO was chosen due to its freedom from polar impurities and unsaturation. It also has a molecular weight and branching close to the most common diluent mineral oil in use today for metalworking fluids.

A steel pin (SAE 3135) was rotated at constant angular velocity (30 radians per second, leading to a tangential velocity of about 10 cm/sec) while being squeezed on opposite sides by two v-shaped steel blocks (AISI 1137) at loads up to 8500 N while submerged in the model lubricants. These are standard test parts for ASTM Method D3233. For seizure load *vs.* concentration determinations, an initial low load of 1180 N was maintained for 300 s (a "break-in" period) before linear loading of the contact with respect to time. Temperature, thermal conductivity and chemical environment were carefully controlled through use of large quantities (1 liter) of well-thermostatted and stirred fluid bathing this cylinder-on-flat, nonconformal tribological contact. The load and torque were continuously monitored as well as lubricant chemistry by Fourier transform infrared (FTIR) analysis of the fluid used for each experiment. Water and oxygen contents were also monitored to determine their effect, if any, on the tribological results; the former was monitored by Karl Fischer titration and the latter by electron paramagnetic resonance (EPR) spectroscopy (2).

Following completion of the initial break-in period, the load applied to the v-blocks was increased linearly as a function of time. The corresponding torque required to rotate the pins at a constant velocity increased proportionately. At some point, however, a sudden, sharp increase in torque during loading was often observed which indicated seizure between the pin and v-block(s); that point was then designated the "seizure load." Under carefully controlled conditions, small bulk fluid temperature changes (independent of viscosity changes) were seen to affect the load at which seizure occurred. The wear rate was also determined, at constant load, time interval and angular velocity, by microscopic measurement of the width of the v-block wear scars. Note that this corresponds to the wear of the antiseizure film from the surface. Straightforward application of cylindrical arc mensuration formulae gave the volume of material, i.e., steel, removed from the v-block. There was typically much less than a 1% decrease in the diameter of the pin so that sliding speeds and distances (for wear determinations) were essentially constant (4).

Surface Analytical Instrumentation and Procedures

Auger Electron Spectroscopy (AES)

Following tribological testing, the pins and v-blocks were soaked in toluene for 36 hours to remove any remaining lubricant. They were rinsed with clean toluene, dried and stored under argon. This most-sensitive surface analytical procedure mandates this precleaning procedure before further Auger analysis of the surface (2). Since toluene-soluble wear residues would be removed by this procedure, consideration must be given to the possible role of the removed species in the tribological contact (1). The chlorine chemistry involved in this work suggests the aromatic solvent toluene to be perhaps the best compromise (5). Nonetheless, the generally higher shear strength inorganic films believed to be most important in preventing seizure during EP lubrication were of primary interest here.

A Varian Auger electron spectrometer measured the KLL transitions of carbon and oxygen and LMM transitions of iron and chlorine. A single-pass, cylindrical-mirror analyzer (CMA) was employed in this instrument for Auger electron kinetic energy measurement. The samples were mounted onto a carousel sample holder which was placed in a vacuum chamber evacuated to 10^{-8} Torr for analysis. The incident electron beam for generating the Auger electrons from the sample had an energy of 3 keV. The sampling depth under these conditions is approximately 50 Å.

Depth profiling was accomplished by Ar ion bombardment ("sputtering") using an ion beam energy of 2 keV and a filament emission current of 20 mA leading to an ion current of 10^{-2} A/m². This was also used to remove the outermost carbon containment layer. This bombardment results in a material removal rate conservatively estimated to be 5 to 20 Å per minute, depending on the nature of the material, e.g., atomic mass, electronic structure, etc. (6). Specifically, the tribologically worn regions were sputtered and showed a decrease in the C, O and Cl signals with time (as expected) at any one spot as the Fe signals increased concomitantly.

X-ray Photoelectron Spectroscopy (XPS)

XPS was used to interrogate surfaces of tribological specimens and iron foils following film growth experiments (1), with about twice the sampling depth as for AES measurements ($\sim 100 \text{ \AA}$). These experiments were performed using a VG Scientific, Ltd., Escalab spectrometer with fast transfer interlock, Mg X-ray source (1253 eV $K\alpha$ radiation) and a 500 mm-diameter hemispherical electron energy analyzer with three-channel detection. The analyzer was set to a pass energy of 20–25 eV. The resulting overall spectrometer resolution was then approximately 1 eV with binding energy shifts reliable to about 0.2 eV. Samples were mounted on a sample stub and placed on a six-position carousel and introduced into the vacuum interlock, which was evacuated overnight prior to introduction into the analysis chamber which was maintained at 10^{-9} Torr during data collection. Iron foils were stored under argon immediately after film growth experiments (1) and directly introduced into the XPS for analysis. Isolation and preparation of wear particles for XPS analysis are described below. Typical count rates of 10,000 Hz were obtained using an X-ray power of 400 W. Slight charging effects were noticed in some cases (implying that any film present was insulating) so that binding energies were generally calibrated to the C 1s peak at 284.6 eV (3).

Scanning Electron Microscopy (SEM)/ Energy Dispersive X-ray Spectroscopy (EDS) Analysis

An ISI SX-30 SEM/EDS (EDAX) system operating at 30 kV was used to examine, photomicrograph and chemically analyze worn surfaces and wear particles. The latter were allowed to collect at the bottom of the lubricant reservoir by settling for a long period of time; excess lubricant was then decanted. The reservoir was then filled with toluene which was thoroughly agitated to rinse the particles which were again allowed to settle. Excess toluene was decanted from the reservoir and the remaining toluene allowed to evaporate at room temperature. After homogenous dispersion of all wear particles generated, a representative sample was then imbedded in aluminum foil for various surface analyses, including SEM/EDS. Particle size distribution (number average) was simply determined from an electron micrograph of a typical region by counting particles of each size range chosen (2). Sampling depths for elemental analysis by EDS are typically 0.1 to 1 μm . The irregularity of v-block wear scars, however (1), also prompted the use of optical microscopy to measure their widths since the SEM did not provide a conveniently scaled field of vision (4).

Raman Spectroscopy

To probe the bulk nature of any films grown on iron or steel surfaces, Raman spectroscopy was found to be particularly convenient for the relatively flat surfaces of the v-block wear scar or iron foils and was sensitive to iron halides and particulate carbon. Spectra were obtained in the back-scattering mode using an argon ion laser operating at 514.5 nm with a power of ~ 1 W. The scattered light was analyzed using a Spex double monochromator and the resulting photons detected in pulse-counting mode using a Peltier-effect-cooled photomultiplier tube. The monochromator was controlled by a microcomputer which also accumulated the data to produce the resulting spectrum.

RESULTS AND DISCUSSION

Seizure-Load Dependence on Concentration and "Type I" Behavior

Seizure load vs. additive concentration curves shown in Fig. 2 were obtained with the pin and v-block apparatus using simple, well-defined chlorinated hydrocarbons added to PAO base oil. Additive concentrations are expressed as chlorine percentage to distinguish molecular differences. It is clear that those differences are great. Figure 3 similarly shows the seizure load dependence on concentration for 1,4-dichlorobutane ($\text{C}_4\text{H}_8\text{Cl}_2$). 1,4-dichlorobutane mimics the C/Cl ratio of many chlorinated hydrocarbons used in commercial metalworking fluids. Its response curve is essentially coincident with that for the least effective chlorinated hydro-

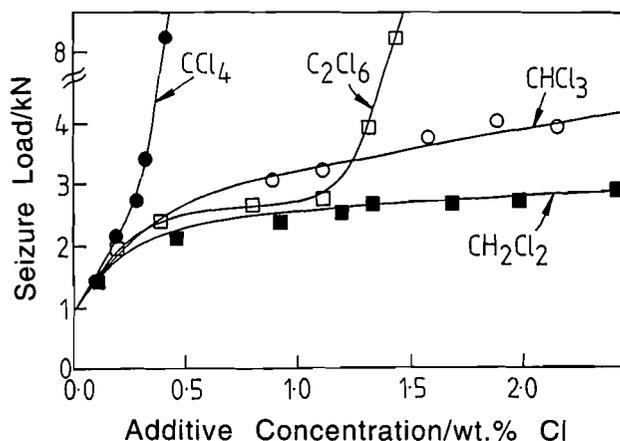


Fig. 2—Plot of seizure load vs. additive concentration (in wt.% Cl) obtained using the pin and v-block apparatus for methylene chloride (CH_2Cl_2) and CHCl_3 (chloroform) which exhibit Type I behavior, carbon tetrachloride (CCl_4) which exhibits Type II behavior and hexachloroethane (C_2Cl_6) which exhibits both Type I and Type II behaviors.

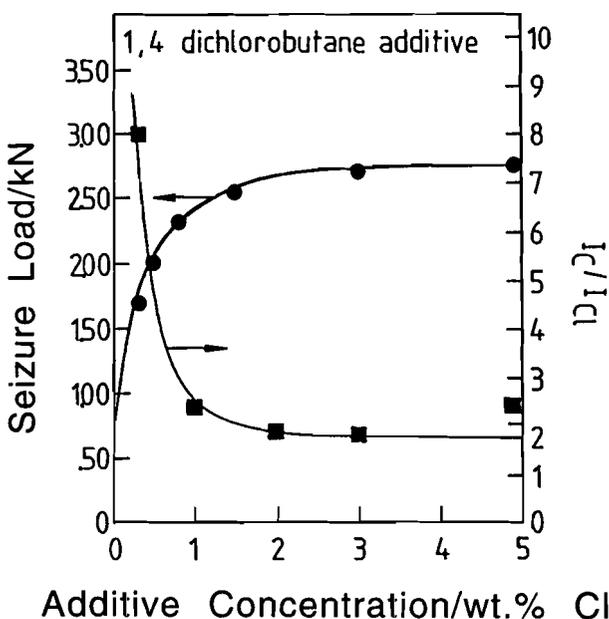


Fig. 3—Ratio of the chlorine-to-carbon Auger signals plotted as a function of concentration of 1,4-dichlorobutane dissolved in hydrocarbon fluid; shown also for comparison is the seizure load plotted vs. additive concentration.

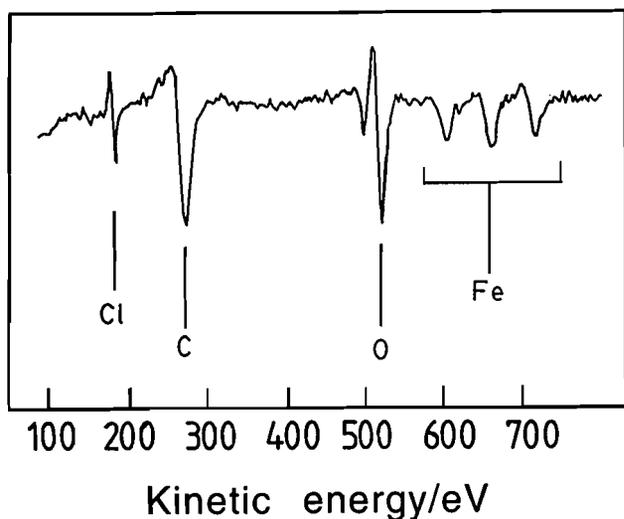


Fig. 4—Typical Auger spectrum (dN/dt vs. KE) of the surface of a pin after the surface contamination has been removed by Ar ion bombardment (2).

carbon shown in Fig. 2, methylene chloride (CH_2Cl_2). As commonly experienced in the past, the now-forbidden carbon tetrachloride (CCl_4) is the most effective EP additive of this class; here less than 1% of it prevents seizure (cold welding) between the pin and v-blocks at all loads possible as compared to nearly 100% methylene chloride (CH_2Cl_2). Except for carbon tetrachloride (CCl_4), all the chlorinated hydrocarbons tested (including commercial additives) showed a "plateau" region or load limit at relatively low concentrations and at approximately the same 2800 N load; these are said to show "Type I" behavior here. Carbon tetrachloride (CCl_4) shows no plateau and is designated "Type II." The statistically significant differences in these plateau levels, as well as differences in chlorine concentration for Type II performance, e.g., 0.5% for carbon tetrachloride (CCl_4) and 1.5% for hexachloroethane (C_2Cl_6) shown in Fig. 2, do not correspond to differences in average C-Cl bond strengths as proposed by others (7), (8).

Analysis of the Tribological Surface

Since surface chemistry appears to be important in the performance of chlorinated hydrocarbons such as EP additives, extensive surface chemical analyses were carried out on the contacting surfaces and wear debris. Figure 4 displays a typical Auger spectrum of the pin surface after having been argon ion bombarded for about one minute to remove surface contaminants. This procedure results in the removal of the outermost 5–20 Å region of the surface. Iron, chlorine, carbon and oxygen are clearly detected. Analyses of the test fluid suggest that the oxygen concentration, both in the form of dissolved oxygen and as water, was very low (2). The presence of the oxygen detected using Auger spectroscopy (Fig. 4) is ascribed to oxidation or hydration of the surface following tribological testing and prior to insertion into the Auger vacuum chamber. Note that adventitious oxygen and carbon are often found together (9). Deliberate saturation of this fluid with oxygen under these tribological conditions revealed no significant effect due to oxygen (10). It should also be pointed out that the tribological run-in procedure removed

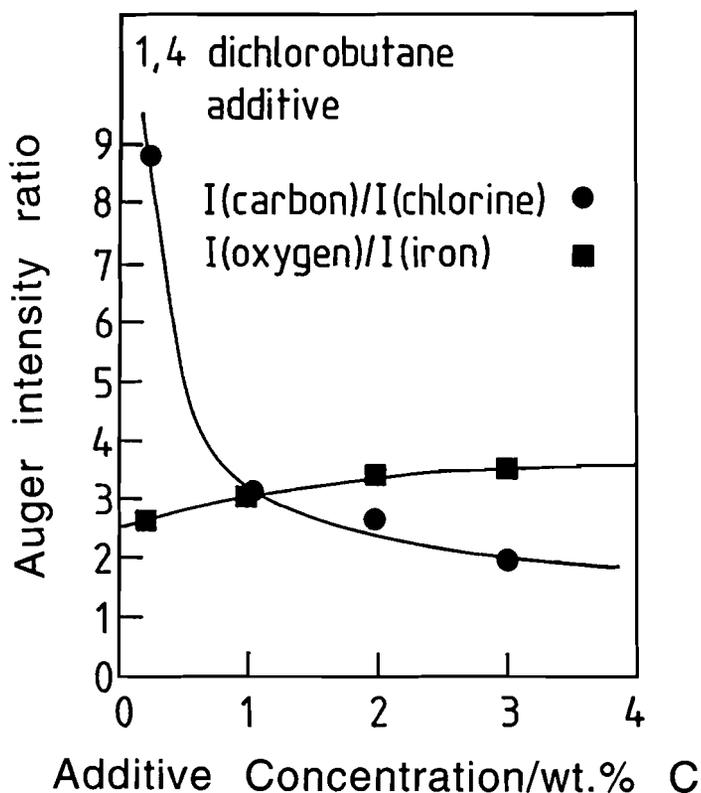


Fig. 5—Auger peak-to-peak amplitude of oxygen normalized to the Auger signal due to iron plotted as a function of 1,4-dichlorobutane concentration; shown for comparison is the ratio of Auger carbon signal to the chlorine signal.

enough of the outer surfaces of the contact region to remove the original oxide layer (usually estimated to be 50–100 Å thick) as well as roughness. In this context, recent work with PAO indicates that, at the interfacial temperatures determined below (>500 K), any oxide films on polycrystalline iron are reduced by the PAO itself (11), (12).

The Auger spectra of the pin surfaces at the point of seizure during linear loading with the pin and v-block apparatus were obtained following lubrication with 1,4-dichlorobutane at relatively low concentrations. The ratios of C:Cl Auger peak-to-peak intensities (I_C/I_{Cl}) are plotted along with seizure load as a function of concentration in Fig. 3 for this Type I behavior. There is a strong correlation between outer surface composition and EP performance. Figure 5 compares this Auger ratio also to the oxygen/iron ratio for these pins, indicating that the oxygen concentration does not correlate with tribological performance. The affinity of oxygen and water for these uninhibited and chlorinated oil-wetted, active steel surfaces is commonly experienced in heavy-duty metalworking by the appearance of a visible bronze-to-reddish brown discoloration within minutes of new surface generation; pure, dry iron chlorides are black or white, depending on the degree of chlorination (13).

X-ray photoelectron spectroscopy (XPS or ESCA for Electron Spectroscopy for Chemical Analysis) was also employed to determine chemical states of the substances found in the surface film. In particular, Fig. 6 shows the Cl region for the particles collected during a typical seizure load determination as compared to other chlorine sources, both inorganic and organic. The latter is represented by the nonvolatile poly-

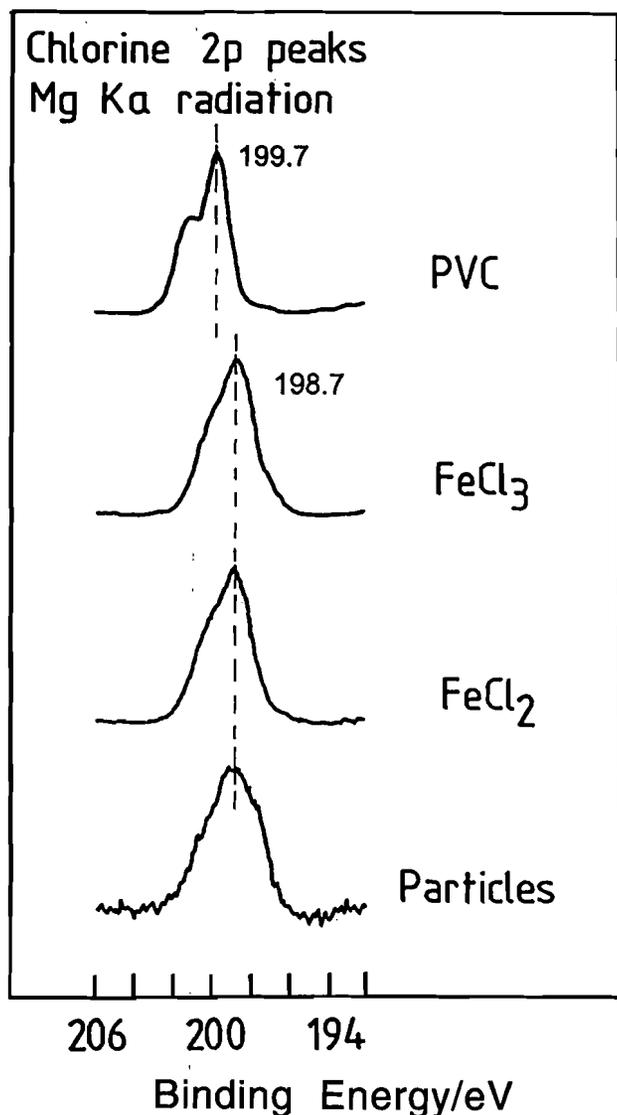


Fig. 6—Cl 2p region of the X-ray photoelectron spectra of polyvinylchloride (PVC), ferric chloride (FeCl₃), ferrous chloride (FeCl₂), and the particles removed during experiments in the pin and v-block apparatus taken using Mg K α radiation. All but PVC show their maxima at 198.7 eV binding energy.

vinylchloride (PVC), a model for the original chlorinated hydrocarbon as well as its possible friction polymers. Note, however, that one cannot rule out the removal of at least some of this possible organic tribological material by the solvent rinse procedure described above. Nonetheless, the data of Fig. 6 clearly indicate that the binding energy for the chlorine present on the particles corresponds to a chloride, thereby indicating chemical reaction between the chlorinated hydrocarbon and steel surfaces under these conditions.

These particles, as well as pin and v-block contacting surfaces, were also examined in a scanning electron microscope equipped with EDS analytical capability for element identification. Depth of analysis in this case is one or two orders of magnitude greater than Auger or XP spectroscopies. Nonetheless, it also reveals the presence of carbon, oxygen and chlorine along with iron in both particles and pin and v-block surfaces. Table 1 shows the effect of the presence of this chlorinated hydrocarbon on composition of the washed particles. Note especially the greater concentration of car-

REGION (kev)	ELEMENT	COUNT RATE (Hz) ^{a)}	
		0% ADDITIVE	5% ADDITIVE
0.23–0.30	C	0.07	0.18
0.44–0.60	O	6.84	5.75
2.54–2.72	Cl	0.25	6.76
6.16–6.64	Fe	527.58	628.45

a) Total counting time was 500 s.

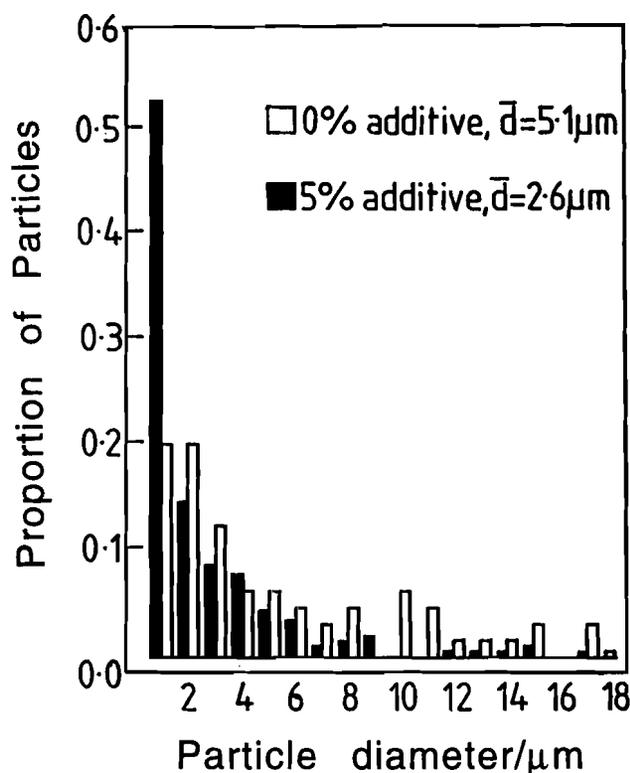


Fig. 7—Histogram of the distribution in sizes of the particles removed from the pins and v-blocks during experiments using the pin and v-block apparatus; the open bars are for experiments using a fluid containing no additive, and filled bars are for a fluid containing 5% (wt.) 1,4-dichlorobutane; number-average particle diameter is also indicated.

bon, as well as the expected chlorine, with the use of this additive to the PAO in spite of the fact that there is a lower total concentration of carbon available in the lubricant (see Ref. (1) for further discussion). The oxygen content is even lower with chlorinated hydrocarbon, more evidence for the lack of oxygen involvement in this tribological situation and for its introduction after the test. Figure 7 also shows a significant diminution in particle size of the wear debris with the addition of a chlorinated hydrocarbon. Again, the particles sampled were representative of the total quantity of wear particles (see SEM/EDS discussion above). Thus, the number-average particle size is about the same order of magnitude as the thickness of films grown from chlorinated hydrocarbons on iron (0.1 to 1 μ m) (1). This is also verified by the total sputtering time (200 minutes at 5–20 \AA per min-

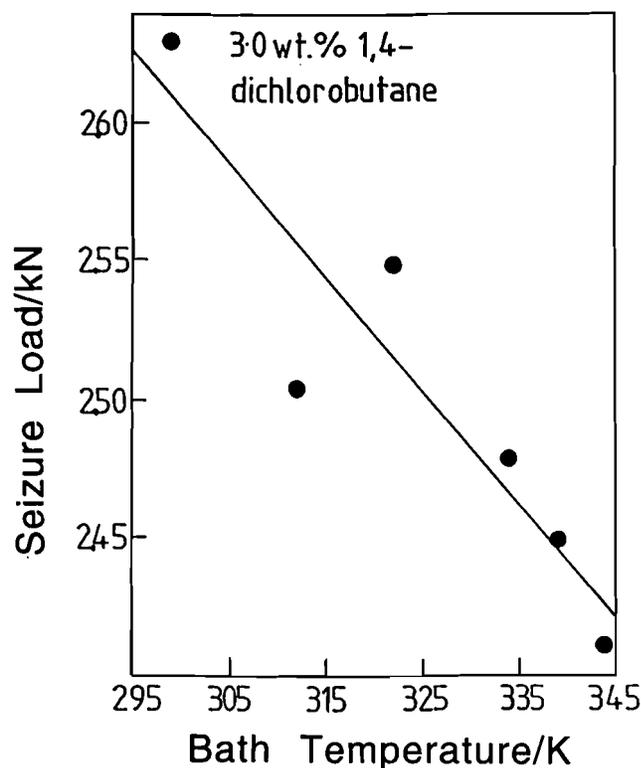


Fig. 8—Plot of seizure load, measured using the pin and v-block apparatus, as a function of bath temperature for 3.0 wt.% 1,4-dichlorobutane ($C_4H_6Cl_2$) dissolved in PAO.

ute) needed to eliminate the chlorine peak in the Auger analysis above (2). Thus, surface analyses indicate that the anti-seizure film formed under EP conditions consists of an iron chloride-like material containing some form of carbon and is $\sim 1 \mu\text{m}$ thick.

Critical Interface Temperature

The nature of the surface alone cannot explain the origin of the Type I behavior for chlorinated hydrocarbons in spite of the observed correlation between seizure load and C/Cl ratio with concentration (Fig. 3). The interfacial temperature estimated using a thermocouple attached close to the interface (Fig. 1) provided evidence of a sharp increase in temperature at the interface where the applied load reached the seizure load in the plateau region (Fig. 2). Such a temperature increase was found for all chlorinated hydrocarbons. Seizure occurred at this point for Type I behavior while, for Type II behavior, the sharp increase was followed by a recovery in the rate of temperature rise more like rates found during initial loading of the pin. Figure 8 also shows the result of a series of experiments to probe the effect of ambient temperature on seizure load. The decrease in seizure load with increasing bath (bulk oil) temperature for even this small temperature range indicated that the rate of film growth, which would increase with temperature, to be less important than the grown film's integrity, e.g., its shear strength. Linear regression on this data allowed determination of a critical temperature for this film, i.e., a temperature at the interface for which loads approaching zero would nonetheless cause seizure. This was rigorously derived elsewhere (3) and found to be $950 (\pm 100)$ K, a range which

includes the melting temperature of the thermodynamically favored chloride of iron, ferrous chloride ($FeCl_2$) (943 K) (14). This result suggests this substance to be the tribologically significant film for Type I behavior. Further, this critical temperature allowed an interfacial temperature/load relationship to be derived for this apparatus under these EP conditions as

$$T(K) = T_0 + 0.25 L \quad [1]$$

where T_0 is the bath temperature (in K) and L is the direct load in Newtons (3). This relation, along with determination of film removal rate as a function of load (L), confirms that ferrous chloride ($FeCl_2$) forms the critical separating film in Type I behavior for all chlorinated hydrocarbon additives.

Fundamental measurements of interfacial temperature as a function of load have been directly made by others for various nonferrous metals rubbing on a steel disc by using the electromotive force generated by the resulting thermocouple (15). Although the authors were prevented by the presence of an insulating film from applying this method to the tribological experiment, it was possible to extrapolate their measured linear relationship between load and temperature (analogous to that shown in Eq. [1]) to yield comparable interfacial temperatures to those measured in the pin and v-block apparatus after making adjustments for metallurgy, sliding velocity, thermal conductivity, apparent contact area and coefficient of friction μ . They express interfacial temperature T as

$$T = T_0 + c(k)\mu v W \quad [2]$$

where T_0 is temperature of the surroundings (bath temperature), v the relative sliding speed, W the load and $c(k)$ a constant function of thermal conductivity k (and emissivity, if any) and geometry of the system (15). This equation is exactly analogous to that given in the appendix of Ref. (16), which is based simply on heat balance for these sliding contacts (assuming all frictional energy loss appears in the form of heat). For the pin and v-block experimental procedure described above, μ and v as well as the analogous $c(k)$ are constant, and their product equals the 0.25 K/N constant of Eq. [1] if the direct load L (analogous to W of Eq. [2]) is in Newtons. As in Fig. 8, the work of Ref. (15) also indicated linearity of temperature with load for all speeds and loads tested until quite close to the melting point of the interfacial material. Here, material removal, due to greatly lowered shear strength near the melting point, controlled the temperature rise so that all temperature *vs.* load (or speed) curves asymptotically approached that temperature (15). This is precisely analogous to the authors' removal curves (1).

It can be anticipated that the methylene chloride (CH_2Cl_2) and chloroform ($CHCl_3$) additives completely thermally decompose under the influence of the relatively large interfacial temperatures attained during extreme-pressure lubrication. This suggests that the relative amounts of chlorine and carbon in the film merely reflect the stoichiometry of the precursor additive. This idea is currently being explored further.

CONCLUSIONS

"Type I" tribological behavior for relatively low concentrations of chlorinated hydrocarbons added to PAO apparently results from reactive film formation with iron. Surface analyses indicate that the film consists of FeCl_2 and carbon. This film prevents seizure between rubbing steel surfaces until its temperature approaches the melting point of ferrous chloride in the pin and v-block rubbing interface. At the melting temperature, its shear strength apparently drops quickly and the film is removed much more rapidly than it can be formed by further reaction. Part II examines the kinetics of film formation and the quantitative aspects of its removal, thereby allowing the modeling of this interface.

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