[Review Paper]

Practical Performance and Action Mechanism of Ester Lubricants in Minimal Quantity Lubrication Machining

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Minimal quantity lubrication (MQL) machining typically uses several tens of milliliters per hour of cutting fluid: a very small quantity compared with generally several tens of thousands of milliliters per hour in the conventional flood supply of cutting fluids. MQL machining can reduce considerably the consumption of cutting fluids, so is a representative and successful environmentally friendly manufacturing operation. Specific synthetic polyol esters with high biodegradability, excellent oxidation stability, and satisfactory cutting performance were evaluated as optimal cutting fluids for MQL machining. The esters are required to work as an effective lubricant in the cutting zone in very small amounts, so the tribological actions are particularly important to improve the cutting performance. A controlled atmosphere cutting apparatus was devised to investigate the relationship between the tribological action and the practical cutting performance of the esters in MQL machining. A model ester and oxygen showed mutually enhanced adsorption activities for machining of steel by the efficient formation of an adsorption film which provided the lubricating effect and improved the cutting performance. In contrast, the presence of oxygen resulted in unfavorable cutting situations for machining of aluminum.

Keywords
Minimal quantity lubrication, Metal cutting, Cutting fluid, Ester lubricant, Tribology, Adsorption activity

1. Introduction

Tribology is significant for environmental preservation, largely through its contributions to energy saving and resource conservation by reducing friction and controlling wear. Lubrication technology is widely used, but more recently environmental problems have been often encountered including the greenhouse effect, human health and safety concerns, oil resource consumption, waste oil disposal and oil leakage. As a result, most current research on lubricants has concentrated on measures to cope with such problems.

Lubricants are generally necessary to achieve high and efficient productivity in the field of manufacturing. For this purpose, cutting fluids are used in most machining processes, but the requirements for environmental preservation in manufacturing processes have resulted in a trend to reducing the amounts of cutting fluids and dry machining is now of great importance. Dry machining is of course the best solution to the environmental problems of cutting fluids, and is successful in many practical manufacturing processes. However, dry machining is sometimes less effective if higher machining efficiency, better surface finish quality, and severer cutting conditions are required. Minimal quantity lubrication (MQL) machining is expected to operate under such conditions.

MQL machining uses a very small amount of cutting fluid supplied to the cutting zone as oil mist particles with a compressed carrier gas. The oil particles provide lubrication, and the compressed gas, normally air, partly provides cooling. Figure 1 shows examples of turning by MQL machining and conventional machining with flood fluid supply. No cutting fluid is visible at the MQL nozzle, but a mixture of oil particles and compressed air is supplied to the tip of the tool. The cutting fluid supply in MQL is typically only several tens of milliliters per hour: a very small quantity compared with the conventional flood supply of generally several tens of thousands of milliliters per hour. Nevertheless, MQL machining provides suitable cutting performance in a number of practical applications. Hence, MQL machining can considerably reduce the consumption of cutting fluids, leading to environmentally friendly manufacturing operations.
Conventional cutting fluids have so far been selected mainly on the basis of their primary characteristics, that is, the cutting performance. In addition, the MQL lubricant should also have secondary characteristics, such as biodegradability, safety, and oxidation stability. Further, MQL machining cutting fluids are required to act as an effective lubricant in the cutting zone in very small amounts, so their tribological action is particularly important to achieve adequate cutting performance.

The present study evaluated specific synthetic polyol esters having high biodegradability, excellent oxidation stability and satisfactory cutting performance as optimal cutting fluids for MQL machining. Using a controlled atmosphere cutting apparatus, this paper investigated the relationships between the tribological action and the practical cutting performance of the esters in MQL machining.

### Table 1  Physical Properties and Biodegradability of Polyol Esters and a Vegetable Oil

<table>
<thead>
<tr>
<th></th>
<th>Polyol ester A</th>
<th>Polyol ester B</th>
<th>Polyol ester C</th>
<th>Vegetable oil D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (40℃) [mm²/s]</td>
<td>19.1</td>
<td>24.8</td>
<td>47.8</td>
<td>35.6</td>
</tr>
<tr>
<td>Total acid number [mgKOH/g]</td>
<td>0.02</td>
<td>0.08</td>
<td>0.60</td>
<td>0.04</td>
</tr>
<tr>
<td>Pour point [℃] &lt; -45</td>
<td>-20</td>
<td>-20</td>
<td>-20</td>
<td>-20</td>
</tr>
<tr>
<td>Biodegradability (CEC L-33-A-93)</td>
<td>100</td>
<td>100</td>
<td>98</td>
<td>100</td>
</tr>
</tbody>
</table>

**2. Evaluation of Lubricant Esters as MQL Machining Fluid**

#### 2.1. Secondary Characteristics

##### 2.1.1. Biodegradability

Biodegradability is the most important factor for the environmental compatibility of lubricants. In general, the base stocks of cutting fluids consist of mineral oils which do not have high biodegradability. In contrast, vegetable oils have high biodegradability, and synthetic esters provide a wide range of biodegradability depending on the molecular structures of the component acids and alcohols. Since most synthetic polyol esters can be regarded as biodegradable and have suitable viscosity for MQL machining, several polyol esters were chosen as lubricants for examination. Table 1 presents their physical properties and biodegradability compared with a biodegradable vegetable oil.

#### 2.1.2. Oxidation Stability

Lubricant mist particles may form a thin oil film on the interior and exterior surfaces of the machine tools during MQL machining. Such thin oil films are easily oxidized to form sticky substances, so MQL lubricants should be stable against thin film oxidation. To simulate thin film oxidation, 5 g of lubricant was dispersed on an aluminum plate with a surface area of 7850 mm² and exposed to air at 70℃ for 168 h. Any change in molecular weight was measured by gel permeation chromatography (GPC) analysis as shown in Fig. 2.

An increase in molecular weight of more than 10% is associated with a sticky feel to the touch. The molecular weight of vegetable oil D increased by 65%, and the film felt very sticky. In contrast, no significant change was observed in the molecular weights of polyol esters A and B and little change for polyol ester C.

Most vegetable oils consist of a number of ester compounds, mainly derived from a combination of glycerin and fatty acids. These vegetable oils are usually liquids at room temperature because the fatty acid structures normally include unsaturated bonds.

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*Fig. 1  Photographs of Turning by (a) MQL Machining and (b) Conventional Machining with Flood Fluid Supply*
Unfortunately, the unsaturated bond is chemically unstable and may easily undergo oxidation polymerization. Consequently, vegetable oil D exhibited a considerable increase in molecular weight, as seen in Fig. 2.

The polyol esters chosen as preferable biodegradable lubricants in this investigation were synthesized from a specific polyhydric alcohol rather than glycerin. Such molecules have greatly improved oxidation stability because of the absence of unsaturated bonds in the fatty acid components, but remain liquid at room temperature. These specific synthetic polyol esters are therefore likely to provide optimal cutting fluids for MQL machining from the standpoint of maintaining a clean working environment.

2.2. MQL Cutting Performance of Polyol Esters

2.2.1. MQL System

A commercial MQL system was used to supply the fluids to the cutting zone. The system generates a mixture of gas and a minimal quantity of lubricant oil mist, with mean particle diameter of about 1 μm. The gas was compressed air at 0.2 to 0.3 MPa. The oil was supplied at 10 to 30 ml/h to the cutting zone through an outer nozzle.

![Graph](https://example.com/graph.png)

*Fig. 2 Results of the Thin Film Oxidation Stability Test*

<table>
<thead>
<tr>
<th>Cutting tool</th>
<th>Cemented carbide or cermet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rake angle</td>
<td>0°</td>
</tr>
<tr>
<td>Clearance angle</td>
<td>0°</td>
</tr>
<tr>
<td>Workpiece</td>
<td>JIS S45C steel</td>
</tr>
<tr>
<td>Cutting speed</td>
<td>200 m/min</td>
</tr>
<tr>
<td>Feed</td>
<td>0.1 mm/rev.</td>
</tr>
<tr>
<td>Depth of cut</td>
<td>1 mm</td>
</tr>
<tr>
<td>MQL supply</td>
<td>Air 0.3 MPa, lubricant 25 ml/h</td>
</tr>
</tbody>
</table>

Table 2 Conditions of the Turning Test

2.2.2. Turning Test

The turning test was carried out to evaluate the cutting performance of fluids under the cutting conditions in Table 2. The cutting performance was evaluated as the coefficient of friction on the tool rake face, obtained by cutting force dynamometry during turning, and the surface finish roughness of the workpiece after the test. KISTLER-type piezoelectric dynamometers were used to measure the cutting forces at a sampling rate of 50 Hz. Table 3 shows the physical properties of the test fluids. Polyol ester A was designated as PE-A. VO was a rapeseed vegetable oil and VE was a vegetable-based synthetic ester. For comparison, a neat type cutting oil (NO) containing an organosulfur extreme pressure additive was also included, but used only by conventional flood supply.

*Figure 3 shows the coefficient of friction on the tool rake face during turning. The results indicate that the cutting performance in MQL machining with esters PE-A and VE was superior to that in dry machining.*

![Graph](https://example.com/graph.png)

*Fig. 3 Coefficient of Friction in the Turning Test*

Table 3 Physical Properties of Test Fluids

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Viscosity (40°C) [mm²/s]</th>
<th>Biodegradability (CEC method) [%]</th>
<th>Sulfur content [%]</th>
<th>Oxidation stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE-A</td>
<td>19.1</td>
<td>100</td>
<td>none</td>
<td>good</td>
</tr>
<tr>
<td>VE</td>
<td>24.8</td>
<td>100</td>
<td>none</td>
<td>good</td>
</tr>
<tr>
<td>VO</td>
<td>47.8</td>
<td>100</td>
<td>none</td>
<td>poor</td>
</tr>
<tr>
<td>NO</td>
<td>35.6</td>
<td>20-30</td>
<td>3.5</td>
<td>good</td>
</tr>
<tr>
<td>Dry</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In particular, even compared with the conventional flood supply of neat type oil NO, the synthetic polyol ester PE-A provided excellent performance for both cemented carbide and cermet tools. On the other hand, MQL machining with vegetable oil VO was not always effective. Evaluation of the cutting performance using surface roughness after turning is shown in Fig. 4, indicating the surface finish quality for MQL using PE-A was better than that using VO.

2. 2. 3. Milling Test

The milling test was used to compare the cutting resistance between MQL machining with PE-A and conventional cutting with flood fluid supply using NO. Figure 5 shows that MQL machining provide much lower cutting resistance than conventional cutting, again demonstrating the excellent performance of MQL machining with synthetic polyol ester PE-A.

3. Adsorption Behavior of Ester

The tribological action of an ester working as an effective lubricant under the severer boundary lubrication conditions depends on metal soap film formed by some strong chemical adsorption onto the sliding surfaces. Such tribological behavior may be extremely important in MQL machining because the lubricant esters should be supplied to the cutting zone in very small amounts, presumably to the low temperature area where the intimate contact between the tool rake face and the chip is reduced near the separation point. A series of fundamental investigations was therefore conducted using the controlled atmosphere machining apparatus to understand the adsorption behavior of a model ester onto freshly cut metal surfaces as described below⁰¹⁻⁰⁴.

3. 1. Experimental
3. 1. 1. Controlled Atmosphere Cutting Apparatus

Figure 6 illustrates the controlled atmosphere cutting apparatus consisting of a cutting chamber, a quadrupole mass spectrometer, a cutting force dynamometer, a workpiece assembly, a cutting tool, and two gas leak valves. The atmosphere in the chamber could be maintained at $5 \times 10^{-3}$ Pa by two turbo molecular pumps. The mass spectrometer monitored the ion currents of gases in the chamber. The ion current is proportional to the mass change of each gas and can be
The workpiece was attached to the spindle and rotates counter clockwise. The cutting tool was installed in a rod which is connected with the cutting force dynamometer. Since this dynamometer was mounted on a servomotor drive, a radial feed motion could be imparted to the tool via the rod through a vacuum seal. The vapor pressure of ordinary MQL lubricant ester is not high enough for introduction into the chamber, so methyl propionate was used as a model ester. Methyl propionate has similar adsorption characteristics to synthetic esters, as the ester bond determines the mode of adsorption. The lubricating action of esters after adsorption is largely influenced by the length and form of the carbon chain structures.

The machining process was orthogonal using metal disks with a width of 1.2 mm. The rotational speed of the disk and the feed rate of the tool were adjusted synchronously to maintain constant cutting speed and depth of cut. Table 4 presents the cutting conditions of the tests. These conditions were determined after detailed examination of preliminary cutting tests.

### 3. 1. 2. Adsorption Activity Measurement

The experimental procedures for measuring adsorption activity were as follows. After inlet and outlet gas flows were balanced, the introduced gas pressure became constant. Machining of the steel disk specimen was then started at a given cutting speed and feed rate to create a clean surface of the metal. Adsorption or reaction of the introduced gas with this freshly cut metal surface would result in decreased pressure as illustrated in Fig. 7(a). A semi-logarithmic linear relationship could therefore be obtained according to Mori’s method as shown in Fig. 7(b)\(^{16}\). The adsorption activity of the gas component can readily be calculated as an absolute value from the slope of this relationship. This calculation provides the same slope even if ion current is used because of the linear relationship with pressure. The adsorption activity is a quantitative measure of the affinity between the gas molecules and the clean metal surface.

### 3. 2. Results and Discussion

#### 3. 2. 1. Adsorption Behavior of Introduced Gases

Figure 8 shows the changes in the ion current values of gases during cutting using methyl propionate as model ester and oxygen gas. During the cutting period of 60 s, the ion current of the ester decreased and then became almost stable, as expected from Fig. 7(a), indicating that the ester was adsorbed onto the freshly cut metal surface. The ion current of oxygen was also reduced with the decrease in ester content, demonstrating that both ester and oxygen were adsorbed onto, or reacted with, the freshly cut surface complementarily.

A high vacuum was maintained in cutting chamber before introducing the gas, but traces of water may have remained in the chamber. The ion current of hydrogen increased just after cutting started, indicating hydrogen generation. There are two possible explanations: emission of hydrogen contained in the steel from the machined surface, and production of hydrogen derived from the chemical adsorption of the ester onto the steel
freshly cut surface.

3. 2. 2. Evaluation of Adsorption Activity

Figure 9 compares the adsorption activity of methyl propionate with that of n-hexane, a representative hydrocarbon. Methyl propionate showed relatively high adsorption activity in both cases with argon and oxygen. The chemically inactive argon was introduced to equalize the partial pressure of the ester in the chamber to that when ester and oxygen are introduced together. n-Hexane show no significant adsorption because hydrocarbons have no polar group to adsorb on the metal surface. Interestingly, the adsorption activity of methyl propionate was increased in the presence of oxygen, suggesting that oxygen can enhance the adsorption of the ester.

To further examine this complementary adsorption behavior of ester and oxygen, a number of tests were carried out with various levels of oxygen in the chamber before cutting, and the adsorption activities were obtained for both ester and oxygen. Figure 10 presents the relationship between these adsorption activities and the ion current values of oxygen before cutting. This relationship clearly shows that a higher amount of oxygen in the chamber resulted in higher adsorption activities of both ester and oxygen, implying mutual enhancement of adsorption activities.

This situation may be very similar to the behavior of a lubricant in MQL machining, because, even near the cutting point, the lubricant particles are surrounded by a large amount of air containing oxygen. Figure 11 illustrates schematically the difference between conventional flood cooling and MQL supply. The reactivity of the lubricant ester is intensified by atmospheric oxygen in MQL machining, leading to the formation of a robust and tribologically effective lubricating film. The mechanism of such adsorption enhancement of esters by oxygen is not well understood at present. One possible reason is that esters are preferentially adsorbed onto metal oxide rather than freshly cut metal surfaces.

4. Influences of MQL Media on the Practical Cutting Performance

To examine whether the above adsorption behavior is actually related to the cutting performance, the influences of MQL media such as lubricant ester and various carrier gases on the practical cutting performance were investigated. MQL machining of aluminum, as well as steel, was included because the application of aluminum and its alloys to automotive part materials is rapidly growing. Aluminum machining, compared with steel, shows highly adhesive characteristics caused by the low melting point and higher chemical reactivity of aluminum, so more effective lubrication is often necessary, despite the lower hardness. Thus, the tribological characteristics of aluminum machining are extremely important, particularly to avoid accumulative transfer on the tool or chip jamming.

4. 1. Orthogonal Machining with Normal Atmosphere Cutting Apparatus

Figure 12 illustrates a normal atmosphere cutting apparatus with exactly the same cutting configuration as that of the controlled atmosphere cutting apparatus of Fig. 6. Orthogonal machining was performed with MQL supply and only gas flow of oxygen, air or nitrogen using this normal atmosphere cutting apparatus, under the cutting conditions shown in Table 5. Figure 13 shows the resultant cutting force obtained by machining of a steel workpiece. MQL machining...
always involved lower cutting force than only gas flow using the same gas, indicating that the ester provided better lubricating effects on the machining phenomena, probably because of adsorption to form a lubricating film. Further, cutting performance improved with higher oxygen concentration in the gas.

The cutting phenomena in MQL machining of steel therefore show tribological relationships with the adsorption behavior of the ester and atmospheric gases. In other words, the experimental observations can be explained by the hypothesis that the adsorption of synthetic esters is enhanced by oxygen, and the resultant efficient formation of a robust lubricating film may improve the MQL cutting performance.

In contrast, the cutting performance for machining of aluminum improved with lower oxygen concentration in the gas, as shown in Fig. 14. The presence of oxygen is presumably unfavorable due to the formation of aluminum oxide (alumina) in the cutting zone. Alumina is extremely hard material, machining is difficult. The main consideration for successful MQL machining of aluminum is therefore how to exclude oxygen from the cutting atmosphere. Another important consideration is that introduction of synthetic polyol ester by MQL mist will always decrease the cutting force compared with only gas flow, even if oxygen is supplied, meaning that a very small amount of the polyol ester acts as an effective lubricant in the MQL machining of aluminum.

### 4.2. Practical MQL Deep Drilling

Deep drilling differs from other open machining operations, in that the MQL mists are usually supplied to the cutting zone from the oil holes of the drill tip, so the atmosphere inside the drill hole can easily become that of the carrier gas. The cutting phenomena in MQL deep drilling may therefore be strongly influenced by the carrier gas.

Table 6 presents the cutting conditions of practical MQL deep drilling test, which were selected after some preliminary drilling tests. The length (hole depth) to diameter ($L/D$) ratios were 10 and 8.3 for machining of steel and aluminum, respectively. MQL mists were delivered through the center of the machine tool spindle and supplied to the cutting zone from the oil holes of the drill tip by a pressurized gas of 0.2-0.25 MPa. Each evaluation test consisted of 100 holes, and the cutting performance was determined as the thrust force.
Figure 15 shows the changes in thrust force of the last 20 holes, that is, the 81st to 100th drilling operations in the case of steel. The values of the thrust force during drilling did not vary so much regardless of the carrier gases. However, negative thrust force was significantly detected, particularly in the case of nitrogen, as in Fig. 15(a), probably because of the inferior axial straightness of the hole. This negative thrust force can therefore provide a measure of the cutting performance. According to this measure, MQL machining with air or oxygen, Fig. 15(b) or 15(c), provided higher performance than MQL with nitrogen, Fig. 15(a). These results of practical MQL deep drilling of steel again agree well with the cutting performance predictions based on the adsorption behavior of the ester and atmospheric gases.

Figure 16 shows the thrust forces during drilling of the last 20 holes in aluminum. As expected, MQL machining with nitrogen, Fig. 16(a), demonstrated low and stable thrust forces, providing more successful cutting compared with MQL ester supplied by air or oxygen, Fig. 16(b) or 16(c). Although these results of practical MQL deep drilling of aluminum are similar to those obtained by the normal atmosphere cutting apparatus, only about 20% of oxygen in air increased the cutting force to the same levels as observed in MQL machining of aluminum with pure oxygen.

These findings suggest that the carrier gas of MQL does not always require a high concentration of oxygen, and this factor must be taken into account for individual MQL machining operations. Better understanding of the tribological behavior, such as adsorption and lubrication, of the esters and carrier gases is necessary to optimize MQL machining for environmentally friendly manufacturing.

5. Conclusions

This investigation has emphasized the importance of secondary performance, such as biodegradability, oxidation stability, and storage stability, for MQL machining fluids. Evaluation of these secondary factors showed that synthetic polyol esters were the optimal fluid for MQL machining. Evaluation of primary performance, i.e., cutting performance, also indicated that the synthetic ester was satisfactory as a MQL machining lubricant. The tribological action of a very small amount of the lubricant is important in MQL machining. Fundamental investigation using a controlled atmosphere cutting apparatus demonstrated that a model ester had preferred adsorption capability on freshly cut metal surfaces, resulting in the formation of a functional lubricating film. Further, the adsorption ability of the ester could be enhanced by oxygen in the cutting atmos-
phere, and this might explain why MQL machining achieves effectiveness.

Such adsorption behavior onto metal surfaces was closely connected with the influences of a synthetic polyol ester lubricant and carrier gases on the cutting performance. In particular, mutual enhancement of adsorption activities by ester and oxygen contributed to the excellent effects on the cutting performance in machining of steel. In contrast, the presence of oxygen resulted in unfavorable cutting situations in machining of aluminum, probably because of alumina formation in the cutting zone. Since the introduction of synthetic polyol ester by MQL mist worked effectively, the main consideration is how to exclude oxygen from the cutting atmosphere in MQL machining of aluminum.

References