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Application of Calcium Carbonate as Green Lubricant Additive in Sheet Metal Forming

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Abstract. The application of calcium carbonate particles as a green lubricant additive for sheet metal forming processes has been evaluated. Different particle sizes were tested, along with different concentrations of particles in a lubricant that typically does not perform well by itself. The lubricant mixtures were tested under pin-on-disc, four-ball, and bending-under-tension test conditions. The results of the different tribological tests were compared to determine whether standard tests, such as the four-ball test, could predict lubricant performance under sheet metal forming conditions. The application of any concentration of particles was shown to be beneficial to the lubricant performance in terms of wear resistance even though friction increased when calcium carbonate particles were added to the base paraffin oil. Small particles (40 nm) exhibited better performance than large particles (2 μm).

Introduction

Lubricants are a vital part of the modern manufacturing industry. They allow increased control over tribological conditions and can help reduce the environmental impact of various processes through waste reduction and improved energy efficiency [1]. The composition of lubricants must be considered carefully as it will define how the lubricant performs as well as how it can affect the environment around it when it is used. The performance of a lubricant is a function of its composition in terms of the base oil, additives and the overall formulation [2].

Various types of lubricant additives are used to tailor the lubricant properties. Metal and metal-oxide particles can be used to improve friction-reduction and anti-wear properties, while various sulphur compounds are used to improve anti-oxidation properties [3]. Mannekote et al. [2] list 10 different types of additives and the function of their application, which ranges from wear-reduction to viscosity index improvers.

Some additives are known to be harmful to the environment, or to humans. In sheet metal forming, additives are typically included to improve the extreme-pressure and anti-wear properties of the lubricant as sheet metal forming processes often experience high contact pressures, which can in turn lead to excessive wear and limited tool-life. The additives that are used for tribologically severe sheet metal forming processes are therefore often based on chlorinated paraffins which are known to be environmentally hazardous [4]. With increasingly restrictive legislation on the use of chlorinated paraffins, the use of alternative, environmentally benign additives is becoming more popular. However, these often contain nitrites or heavy metals, which are known to be harmful to aquatic life and human health [5] and can therefore not be seen as a permanent solution to this problem as it is likely that future legislation will restrict their usage.

Sheet metal forming represents a set of challenging tribological conditions and as such, lubricants must be tested specifically under these conditions to ensure that they are suitable. Standardized tests, such as four-ball testing, can be used to gauge lubricant performance under model conditions. For any sort of quantitative evaluation however, it is necessary to simulate sheet metal forming conditions more directly, such as by utilizing simulative tests [6].

In this work, two standardized lubricant tests are used, along with one simulative test to gauge the suitability of the application of calcium carbonate particles as a green lubricant additive for sheet metal forming. The results of the standardized tests are compared to the simulative tests to evaluate how well the standardized tests can predict lubricant performance under sheet metal forming conditions. Calcium carbonate is not ecologically harmful, nor is it of concern to human health under the conditions that it is used here [7]. It has already been shown to improve various lubricant properties in simulative tests [8] as well as a production test [9]. It may work as an alternative for chlorinated paraffin oils, which are still used today where extreme-pressure properties are necessary.

Background

Various investigations of the application of particle additives to improve lubricant properties have been performed. Mixtures containing different particle sizes and base lubricants have been put through various tribological tests to determine how the lubricant properties are affected, and the typical outcome is that the lubricant is improved compared to the base lubricant, at least when calcium carbonate is used. Table 1 shows an overview of some investigations that are based on using calcium carbonate as a lubricant additive. It is clear from the table, which is not exhaustive, that a wide variety of tribo-conditions have been used to test different mixtures of various particle sizes and base oils.

Table 1: Overview of investigations that have involved calcium carbonate as a lubricant additive.

Ref.	Particle size	Base lubricant	Tribo-conditions	Result
[5]	45 nm	Lithium grease	Four-ball test	Reduced wear and friction
[8]	40 nm	PAO	Ball-on-block	Reduced wear and friction
[9]	1 μm	Lithium grease	Hot rolling	Improved process stability
[10]	200 nm	Rapeseed oil	Four-ball test	Reduced wear and friction
[11]	4 μm	15# Machine oil	Three-ball test	Reduced wear and friction
[12]	40 nm	40CD oil	Four-ball test	Reduced wear and friction
[13]	< 15 μm	PAO	Ball-on-disc	Reduced wear

The base oil in the lubricant formulation also affects the tribo-pair, but in this work only a pure paraffin oil is considered as it does not exhibit good lubrication properties by itself. Paraffin oil is often used as a base oil in the formulation of lubricants but is not normally used in forming processes without the addition of several film forming additives. Further, it is widely available, inexpensive, and is classified as not being hazardous to the environment [14].

Particle-based additives have been used before to improve the friction or wear resistance properties of tribo-systems. This improvement in properties has been explained in various ways depending on the geometry of the particles. For spherical particles, these explanations range from the formation of tribo-films on the contacting surfaces and rolling being promoted over sliding [15] to reduce wear. In this work, two mechanisms that would reduce wear compared to using only a liquid lubricant are considered. An overview of the mechanisms is given in Fig. 1. In the case of only liquid lubrication being used, and especially at high contact pressures, there is only hydrostatic pressure build-up and hydrodynamic effects that prevent direct contact between the two mating surfaces, which leads to a relatively high level of wear. When particles are added, the size of the particles relative to the surface roughness of the contacting surfaces is important. If the particles are relatively large compared to the surface roughness of the rougher surface, the particles can be trapped in valleys on the surface and prevent asperities from contacting one another to reduce wear. These particles may also be free to rotate, and thus promote rolling instead of sliding. If the particles are relatively small compared to the surface roughness, then they may fill up spaces between asperities, making the surfaces apparently smoother and thus reducing wear. This mechanism is known as surface mending.

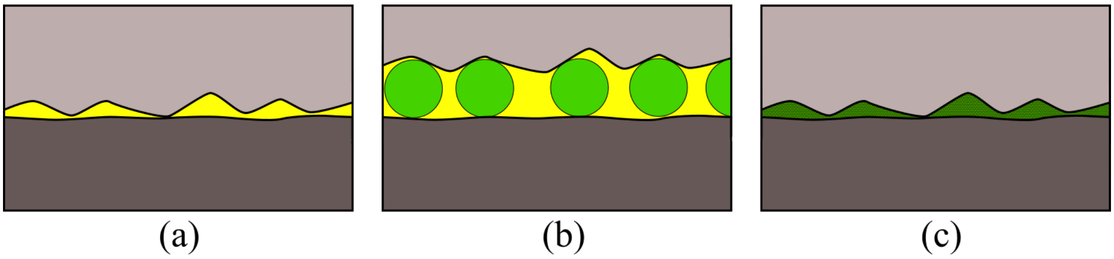

Figure 1: Wear improvement mechanism of particle additives trapped between workpiece (light-grey) and tool (dark-grey). (a) No particles, (b) large particles, (c) small particles.

Various particle sizes of calcium carbonate have been investigated for use as lubricant additives. Depending on the size of the particles relative to the surface roughness of contacting surfaces, the particle action will be different cf. the discussion above. For that reason, two particle sizes are tested in this work. One that is large relative to the surface roughness, and another that is small relative to the surface roughness. This should ensure that both mechanisms outlined above are seen.

Depending on the tribological conditions, the performance of the particles in the lubricant will be different and a different optimal concentration can be found [8]. Under hot rolling conditions, Shimotomai et al. [9] found that a concentration of 60 wt% was optimal for reducing the chance of seizure, whereas Ji et al. [5] found that a concentration of 5 wt% was optimal for wear reduction under four-ball testing conditions. This necessitates testing of various concentrations to ensure that the analysis accounts for the tribological conditions.

Experimental Methods and Equipment

Lubricant mixtures. Lubricant mixtures were prepared before testing by adding paraffin oil to an existing mixture of paraffin oil, Tween60 surfactant and calcium carbonate particles. Two mixtures were used in this work, one having a particle size of 2 μm and the other having a particle size of 40 nm. These are referred to as the large particle mixture and the small particle mixture, respectively. The preparation of a lubricant mixture was performed using a milligram scale, ensuring that the actual concentration is within a 1% deviation from the nominal value that is reported here.

The performance of the lubricant mixtures was evaluated by tribological testing. Two standardized tests, the pin-on-disc (POD) and four-ball (4B) tests were used to evaluate the lubricant performance in standard conditions. A bending-under-tension (BUT) test was then used to evaluate the lubricant mixture performance specifically under typical sheet metal forming conditions.

The range of concentrations that was tested was not the same between the different tests. The pin-on-disc test was performed for concentrations of up to 11 wt% as literature shows that the optimal concentration for friction reduction is generally relatively low as that prevents aggregation of particles from affecting the friction measurements [16] and an over-abundance of particles from locking each other in place to promote sliding over rolling [11]. For more extreme conditions and heavier tribological loads, the concentration was increased up to 40 wt% as process tests have shown that a much higher concentration is necessary [9].

Pin-on-disc testing. POD testing, the principle of which is shown in Fig. 2, was performed on a standard TRB tribometer from CSM Instruments. The test parameters were constant through all tests, with the applied load being 10 N, the sliding speed being 50 mm/s and the final sliding length coming to 100 m. The POD test was applied to determine whether the coefficient of friction between the pin and disc changes as a function of the concentration of particles in the mixture. Relevant components were cleaned in ethyl alcohol before testing. The disc component was made from Vanadis 4E, hardened to 62 HRC and polished to Ra=0.06 μm, whereas the pin component that contacted the disc was a Ø6 mm, AISI304 ball, with a hardness of 25 HRC. The purpose of choosing this material pair was to use a contact pair that may be seen in industry. During testing, the disc was held inside a stage that was filled with lubricant (7-8 ml) to ensure ample lubrication in the contact interface. Each test was repeated three times, with the reported values being an average of the three repetitions.

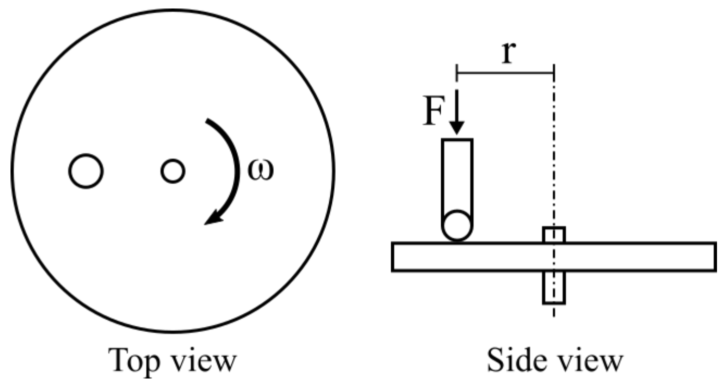

Figure 2: Principle of the pin-on-disc test. A pin is pressed into a disc under a load F at a distance r from the centre of the disc. The disc is rotated at a velocity ω to impose relative sliding between pin and disc.

Four-ball testing. Fig. 3 shows the principle of the four-ball test, which was used to evaluated the anti-wear properties of the lubricant mixtures. The testing was performed according to ISO20613:2018, using a four-ball testing machine that measures applied load, rotational velocity of the motor, and torque. The balls, which were made from a AISI 52100 chromium steel, were nominally the same, having a diameter of 10.7 mm and a surface finish of G20. All tests were performed using the same test conditions: a running time of 60 minutes, an applied load of 300 N and a rotational velocity of 1,420 rpm. The volume of lubricant that was applied, 10 ml, was enough to cover the clamped balls to a depth of about 3 mm, ensuring ample lubrication in the contact interface. Each test was repeated three times, with the reported wear scar diameter being an average of measured values from the test repetitions.

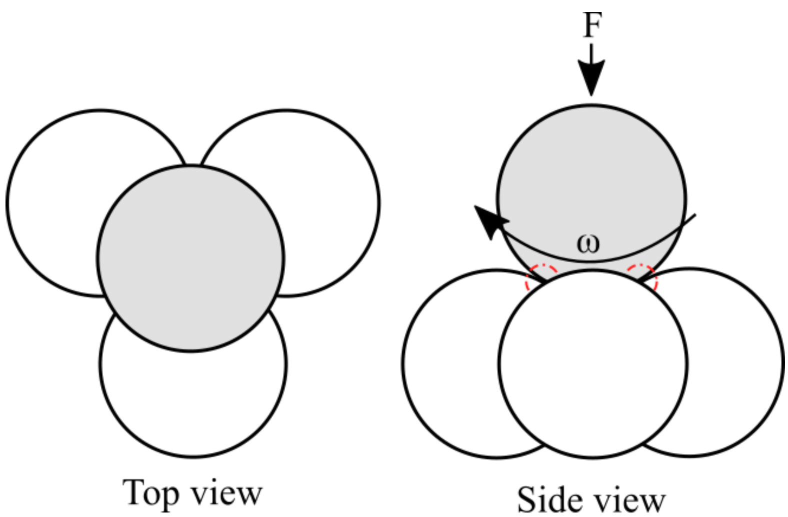

Figure 3: Principle of the four-ball test. Three balls are clamped in a cup so that they cannot rotate. A fourth ball is pressed into the centre of the clamped balls under a load F, and then rotated at a velocity ω to impose sliding in areas marked by red, dashed circles.

Bending-under-tension testing. The lubricant suitability for use under typical process conditions in sheet metal forming was evaluated by BUT testing, the principle of which is shown in Fig. 4(a). The tests were performed on a universal sheet tribo-tester [17]. This test is a simulation of mild tribological conditions that involve medium normal pressure, low sliding lengths and no surface expansion. An example of this is the interface between die radius and cup flange during deep drawing [6]. By monitoring the force necessary to draw the strip over the tool-pin it was possible to evaluate the severity of wear that has occurred on the tool-pin surface, and therefore the capacity of the lubricant mixture for preventing wear [18]. Fig. 4(b) shows one of the tool-pins that were used for BUT testing along with its basic dimensions. The tool-pins were made from Vanadis 4E, hardened to 62 HRC and polished to Ra=0.06 µm. The strip was 30 mm wide and 1 mm thick AISI304 stainless steel with a 2B surface finish. Test parameters were kept constant through all tests: drawing speed of 30 mm/s, drawing length of 20 mm, back tension of 120 MPa and an idle time of 0.8 s between strokes. Each test was repeated twice to account for the reproducibility of the set-up.

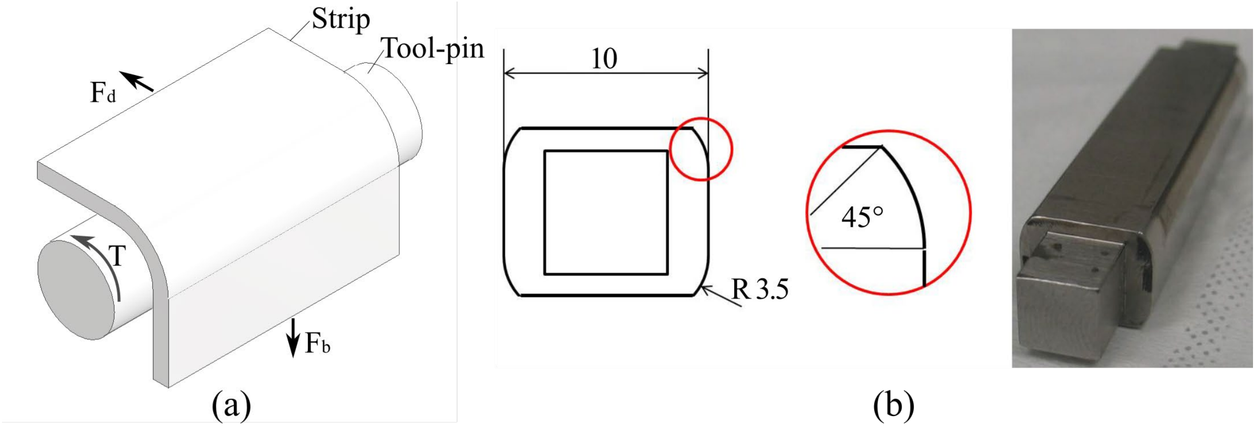

Figure 4: Principle of BUT testing. (a) A strip is bent over a tool-pin under a back-tension F_b. The drawing force F_d and torque T are measured and used as an indication of tool wear. (b) Geometry and appearance of tool-pin used in this work [17].

Measuring equipment. An Olympus LEXT4000 confocal laser microscope was used to evaluate the surfaces of tool-parts and to image the wear scar that was formed during four-ball testing. The images were then processed using SPIP 6.7.7, an image processing software.

A standard Keyence light optical microscope was used to photograph the edges of tool-pins before and after BUT testing.

Results and Discussion

Pin-on-disc testing. POD testing was performed for concentrations in the range 0 – 11 wt% for both particle sizes. During the test, the friction force was recorded, allowing for the friction coefficient to be determined over the course of the test. The average of the three tests was taken as representative for the concentration, leading to the plot shown in Fig. 5.

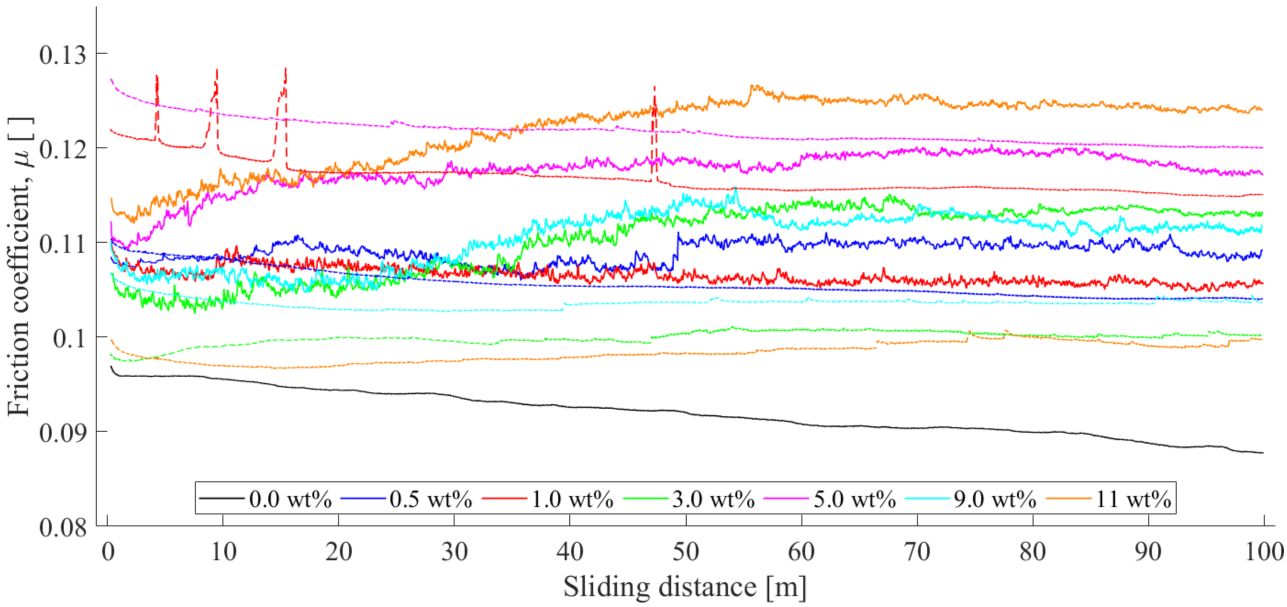

Figure 5: Averaged friction coefficients as function of sliding length for different concentrations of particles. Solid lines represent large particle tests, whereas dashed lines represent small particle tests.

The base lubricant shows a decreasing friction as function of sliding distance. This can be attributed to running-in wear in the form of material transfer to the disc surface and smoothing of the pin surface by asperity interaction. With time this should reach a plateau as running-in finishes, but this supposedly happens after the 100 m sliding distance that was used here. In the same line, the nanoparticles generally show the friction slightly decreasing over the sliding length. This may indicate a similar mechanism, where the surface becomes smoother with sliding. In this case, cf. previous discussion, this would be due to the nanoparticles filling asperity valleys. Depending on the particle size, the profiles look different. The profiles that derive from using small particles are smoother than the ones found when using the large particles. This may be due to the mechanism explained above, where the small particles will artificially smoothen the surface and lead to a more stable friction profile. On the other hand, the large particles get trapped between asperities, and when they are forced to move, they do so by jumping out of the asperity valleys, leading to the fluctuations in the profile. Based on this, the small particles lead to a more stable process.

Fig. 6 shows the average coefficients of friction, taken at stable regions of the profiles shown in Fig. 5, as a function of the concentration that is used. The friction was not reduced, but instead increased by adding calcium carbonate particles to the base lubricant. There was no marked difference between the particle sizes for this behaviour, except for the highest concentration used in these tests of 11 wt%, where the small particles lead to a slightly smaller friction coefficient.

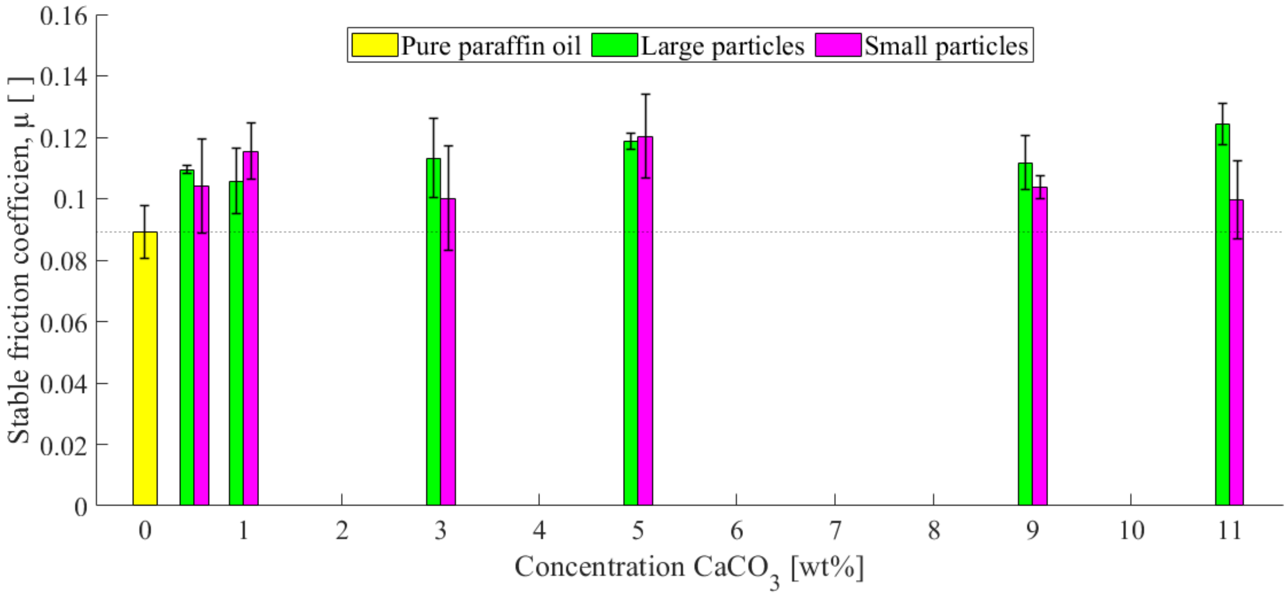

Figure 6: Average friction coefficient as function of different concentrations of particles. Error bars are ± 1 standard deviation.

Four-ball testing. 4B testing was performed for particle concentrations between 0 and 40 wt% for large and small particles. After testing, the wear scar on the surface is imaged for measuring the wear scar diameter. An example location of the wear scars, and a typical wear scar are shown in Fig. 7, along with how the wear scar diameter is evaluated. The measured wear scar diameters are plotted as function of the concentration for both particle sizes in Fig. 8.

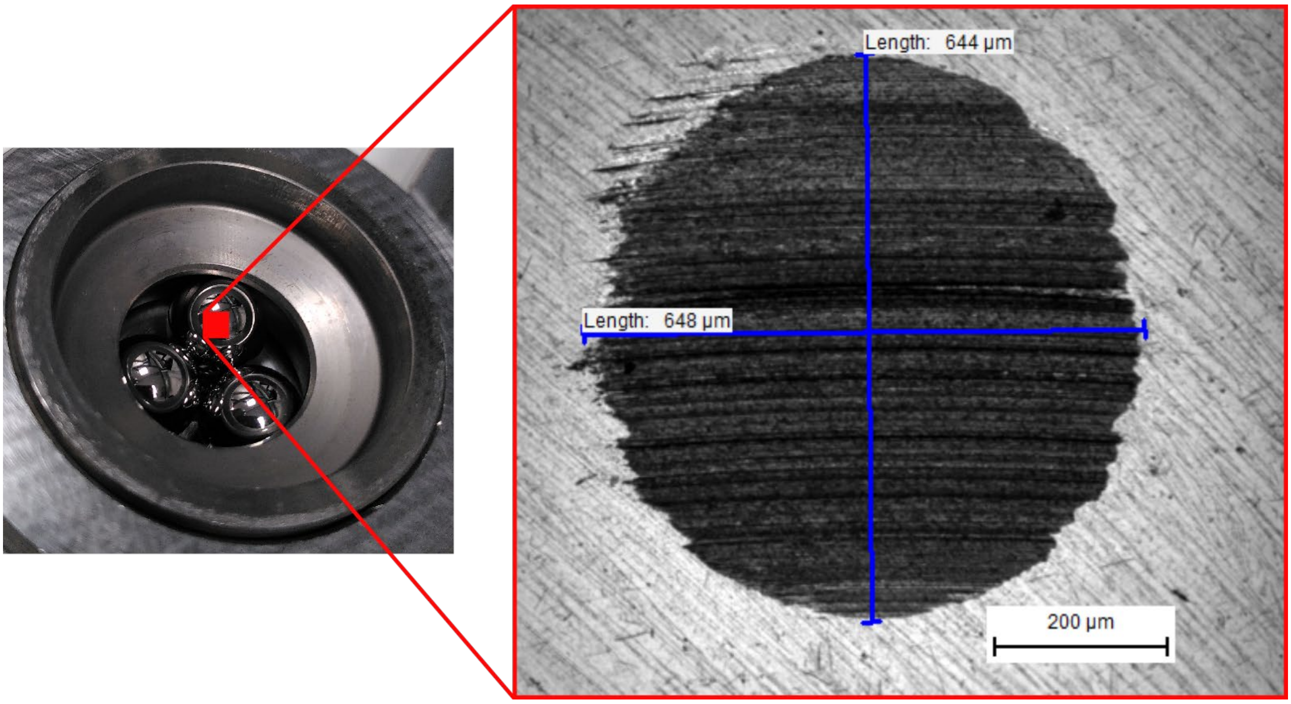

Figure 7: Example location of wear scars (left) and typical wear scar (right).

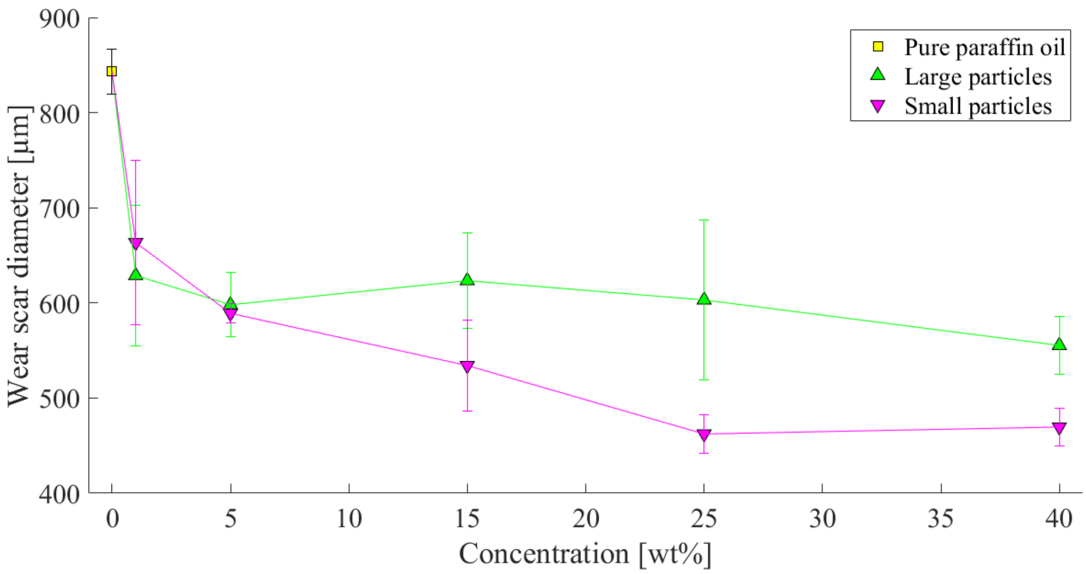

Figure 8: Average wear scar diameter as function of different concentrations of particles. Error bars are ± 1 standard deviation.

For even a concentration of only 1 wt% of particles of either size, the wear scar diameter was significantly reduced. As the concentration was increased, the wear scar diameters that are found for the smaller particles are markedly smaller than the ones found for the large particles. Between the 25 and 40 wt% concentrations of small particles, the wear scar diameter appeared to be plateauing, indicating that the surface is saturated and that the lubrication mechanism has enough particles to work but not too much so that sliding is promoted over rolling [11].

Bending-under-tension testing. BUT tests were performed for concentrations in the range of 0 to 40 wt% for both particle sizes. The drawing forces measured during the tests are shown in Fig. 9 as a function of the number of strokes that have been performed. As can be seen, the pure paraffin oil test was not run to completion as the strip fractured after only 330 strokes in one case and 160 in the other case. All other tests were run to completion, or a total of 1,000 strokes, with the drawing force slightly increasing over the duration of the test. Small fluctuations in the profiles can be explained by the finite length of the axes on the tribo-tester that is used in this work. The variation is caused by the different axes having to reset, one of which resets every 10 strokes and the other which resets every 20 strokes. This is consistent between all tests and should not affect the comparison.

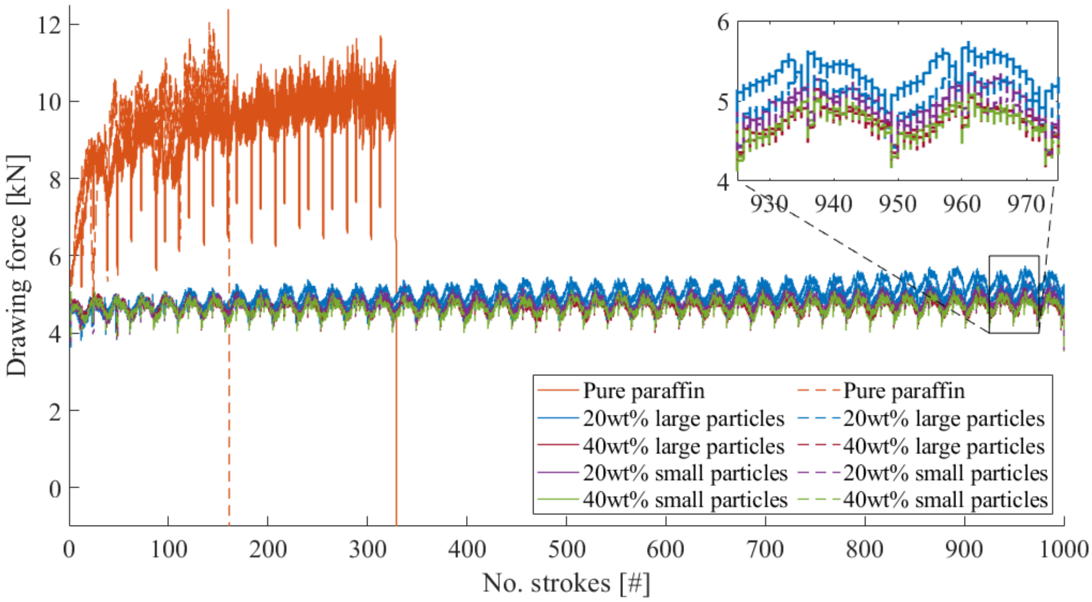

Figure 9: Drawing force as function of number of strokes for different concentrations of particles.

To emphasize the difference between the particle mixed lubricants, a linear fit was found for each of the profiles, excluding the pure paraffin oil. The linear fits were then normalized with respect to the initial drawing force, leading to the plot shown in Fig. 10. It is clear from the linear fits that there is an improvement in using a higher concentration of particles of either size. The 20 wt% concentration of large particles had the steepest slope, which means that the lubricant mixture is less adept at resisting wear. The 20 wt% of small particles was an improvement over the large particles, having a smaller slope. The 40 wt% of either particle size had approximately the same slope, at least it was not markedly different. The normalized drawing force only increased by about 0.01 over these 1,000 strokes indicating that there was very little change to the surface of the tool-pin.

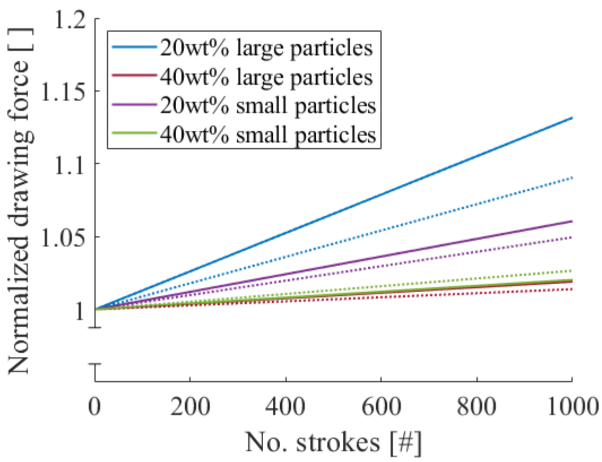

Figure 10: Linear fit to drawing force profiles, normalized with respect to initial drawing force. Dotted lines are repetitions of solid lines of the same color.

After tests were run, the tool-pins were cleaned using paper towels and acetone which removed most of the lubricant mixture. Without further investigation it is impossible to speak to particles that may be embedded in the surface of the tool or workpiece. Fig. 11 shows the used edges of tool-pins that were used for the different tests. The worn edge was similar between repetitions, so only one edge is shown here for each concentration. The wear that occurs on the tool-pins was not quantified, although it is likely to be chiefly adhesive deposition of the stainless steel on the tool-pin surface. The wear scar is clearly most severe for the pure paraffin oil, which explains why the test could not be run to completion. The wear is decreased for the 20 wt% large particles, although it is still visible. For the 40 wt% large particles the wear decreased further, although traces of wear are still visible. Comparing the 20 wt% large and 20 wt% small particle tool-pins shows that the smaller particles are more suitable for decreasing wear at this concentration. The 40 wt% of small particles has very little visible wear, and in fact looks very similar to the unused edge. It is not possible to conclude on whether the 40 wt% of large or small particles performs better from the profiles in Fig. 10, but from looking at the worn edges however, the small particles performed better.

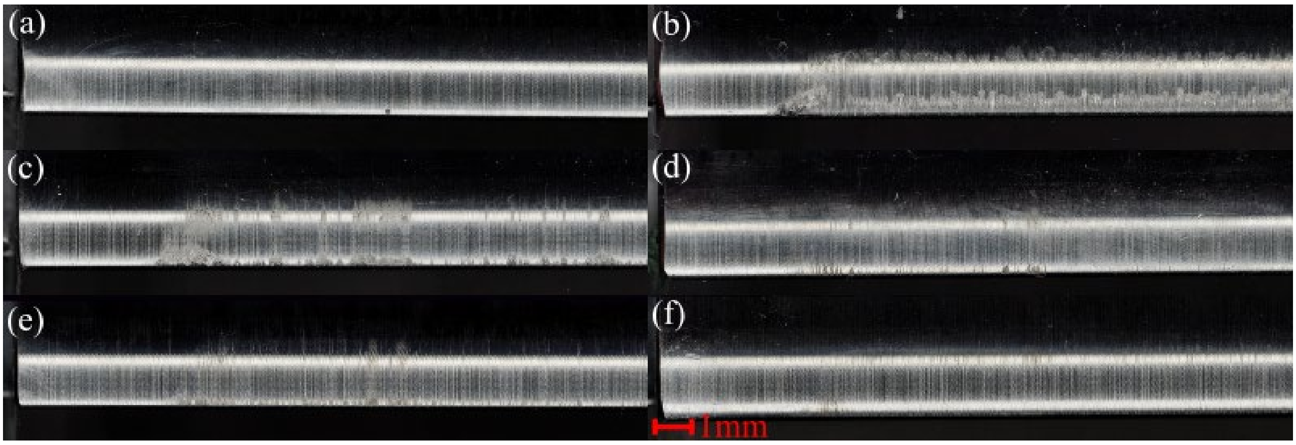

Figure 11: Pictures of tool-pin edges. (a) is an unused edge, (b) was used with pure paraffin oil for 330 strokes, (c) and (d) with a 20 and 40 wt% concentration of large particles respectively for 1,000 strokes, (e) and (f) with a 20 and 40 wt% concentration of small particles respectively for 1,000 strokes.

Conclusions

According to the presented results and discussion above, the following conclusions can be drawn:

- Calcium carbonate can be applied as a lubricant additive to improve the wear resistance of lubricants used under sheet metal forming conditions.
- Standardized four-ball tests show a similar tendency to simulative tests, showing that the four-ball test method is useful as an indicator of lubricant performance under sheet metal forming conditions.
- The anti-friction properties of the lubricant are *not* improved by adding calcium carbonate particles of 40nm or 2 µm size in concentrations of 0 – 11 wt%.
- Smaller particles are useful for stabilizing the contact interface, as was seen in the POD test results.

Calcium carbonate is a viable alternative to environmentally hazardous anti-wear lubricant additives. It is unlikely to be restricted in its usage in the future, as it is not harmful to life or the environment.

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