



Serbian Tribology
Society

SERBIATRIB '13

13th International Conference on
Tribology



Faculty of Engineering
in Kragujevac

Kragujevac, Serbia, 15 – 17 May 2013

POSSIBILITY OF REPLACING THE CHORINATED PARAFFINS IN METALWORKING FLUIDS

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Abstract: All components that are used for neat oil formulations for metalworking operations belong to group of chemicals that, because of its direct application, can have a big influence on the environment and especially on human health.

With time, metalworking operations become more complex and demanding. New materials with various compositions are processed, and they demand metalworking fluids with improved antiwear properties and that provide extreme load-carrying capabilities.

Exactly these additions, known as EP additives, that had been until recently based on chlorinated paraffins, are a group of chemicals that need to be replaced as soon as possible with a components that are environmentally acceptable.

In this paper, in laboratory conditions, we investigated synthetic polymeric esters, as one of the possible substitute for chlorinated paraffins, in several neat oil formulations, which are used for various metalworking operations. From the above comparative results of analysis results it can be concluded that synthetic polymeric esters can serve like an adequate substitute for metalworking fluids which are designed for easy operations.

Keywords: neat metalworking oil, environmentally acceptable lubricants, EP additives, chlorinated paraffins, synthetic polymeric esters.

1. INTRODUCTION

Formulation of industrial lubricants, depending of performance that lubricants must have, requires a lot of different types of additives. Their role in the lubricants is to improve certain characteristics of lubricant or to give the lubricant brand new performance. Usual types of additives are: corrosion and oxidation inhibitor, antifoaming, viscosity index modifier, pour point depressant, antifricition and antiwear additive and additives that allow carrying heavy loads, usually called EP additives.

That large number of additives in particular lubricants formulation lead to a questions not only about the effect of additives in the lubricants, but also the influence of one additive to the another.

Complex testing of antagonism and synergism of all components on particular characteristics in different lubricant formulations are being made. It

can sometimes induce a big problem, especially in recent times, when many components, due to unfavorable effect on humans and environment, are being completely banned for usage in lubricants, or their allowed dosage is greatly reduced.

Research of new environmentally acceptable components and their influence in the lubricant has started many laboratory tests and in the same time tests of their applications in service.

Analyzing the results of one survey, which the editorial of scientific magazine Tribology & Lubrication Technology made, on the question at which additive has the most influence on performance characteristics of lubricants, showed that the answer was EP additives. [1]

The subject of investigation in this paper is testing the antiwear and EP characteristics of different formulations of neat oil for metalworking operations, which in its composition have EP additives. Exactly this extras, known as EP

additives, that had been, until recently, based on chlorinated paraffins are a group of chemicals that needs to be replaced as soon as possible with components that are environmentally acceptable.

In this paper, in laboratory conditions are prepared samples of several different formulation of neat oil which are intended for different metalworking operations. Among the other standard characteristics, are also tested antiwear and EP characteristics of samples containing synthetic polymeric esters, as one of the possible replacement for chlorinated paraffines. The results of analysis are compared with the results of the samples that are formulated with chlorinated paraffins.

2. EXTREME PRESSURE (EP) ADDITIVES

Primary functions of metalworking fluids are heat control, cooling the surfaces of tools and parts processed in the cutting zone and lubrication and enduring the extreme pressures and heavy loading during processing. It is particularly important in order to achieve desired size, shape and degree of surface processing of workpiece, and longer tool lifetime. Removal of cuttings from operating zone is considered as secondary role, but it is very important and it needs to be done continually. Corrosion protection of tools, machines and workpieces is also important. Freshly processed metal have tendency to corrode faster during machine operations, than protected metal.

For metalworking it isn't enough to use only one kind of lubricant, but every applicable process requires specially formulated oil. In order to emphasize differences in characteristics of certain lubricants, in this case, of neat oils, and point out the complexity of choosing the basestocks for formulations, we start with metalworking processes, which are:

- Removal (formation of cuttings), mostly named cutting operations
- Shaping: pressing, rolling, drawing...
- Treating (surface strengthening): quenching
- Protection (corrosion protection: temporary with interprocess, during transport...)

Cutting operations can be considered as the most common in metalworking operations. Basic methods of metalworking cutting are:

- Scraping
- Planning (during operation it is identical to scraping, but the process is discontinuous)
- Drilling (beveling, widely considered: drilling, widening, reaming)
- Milling (oblique and orthogonal cutting)
- Grinding (removal of thin layer of material during the finest final processing)

Operations of metal forming, such as: pressing, rolling, drawing (wire, profiles) are also very used and are considered as demanding.

2.1. EP additives and their role in metalworking fluids for heavy operations

Traditional additive packages that are added to neat metalworking oils in the boundary lubrication regime remain on the metal surfaces and they cannot prevent increased friction, wear and the damage to the tool. EP additives are needed to enable the application in the more difficult conditions of elevated temperatures and pressures.

The main groups of EP additives are:

1. Chlorine compounds
2. Phosphorus additives
3. Sulphur additives
4. Prebasic sulfonates (calcium and sodium)

The first three EP additives are activated in reactions with the metal surfaces in a certain temperature range. Chlorinated additives are activated at temperatures between 180 i 420 °C, phosphorus are activated at higher temperatures and sulphur at even higher temperature range which ends at 1000 °C. In the reaction with the metal surface these three types of additives produce Fe-chloride, Fe-phosphide and Fe-sulphide, which serve as a barrier to reduce friction and wear and elimination of welding.

The fourth EP additive, prebasic sulfonate, act by other mechanisms, whose process doesn't depend on temperature, and operate below 500 °C.

In each category of EP additives there are several different types. The main used chlorinated additives are chlorinated paraffin, or even called a chlorparaffine. In case of phosphorus compounds, the most common type is phosphate ester. With sulphur additives those are: sulphurated fats, sulphurated esters, sulphurated hydrocarbons and polysulphide, which differ in the concentration of free (active) sulphur.

In order to select EP additive in formulations for metalworking fluids, one must be familiar with the applications itself, machining operations, state of the tools and to have defined expected performance. One of the most important information is the possibility of early cancellation of tools before the operation has reached the right temperature for EP additive to become activated. Besides the choice of EP additive, it is necessary to know the synergism with other additives included in the formulation, and also to reduce undesirable interactions which can bring to instability of product using certain combination (foaming, sludge).

The greatest influence on the formulation of neat oils for heavier operations was limiting the chlorine content. For manufacturers of these substances it was hard task to find an adequate replacement in a very short period of time.

Many studies have been done on the impact of chlorinated paraffins on the environment, and it reached its expansion in mid-nineties.

Chlorinated paraffins are divided in three classes based on the chain length:

- Short-chain, C₁₀₋₁₃
- Medium-chain, C₁₄₋₁₇
- Long-chain, C₁₈₋₃₀

The most commonly used chlorinated paraffins were with 35-70 % of chlorine and with the hydrocarbon base with C₁₀₋₂₀.

These studies have shown that short-chain chlorinated paraffins have the biggest potential risk of influence on the environment especially if they are not handled properly when they become waste material.[2]

In summary, therefore, the lists of undesirable chemicals in the formulations of many metalworking fluid include one of the most commonly used EP additives, chlorinated paraffin.

Chlorine in lubricants, at elevated temperatures and pressures reacts with hydrogen, and forms hydrogen chloride and dioxine, and dissolving hydrogen chloride in water forms hydrochloric acid.

A special problem brings the impossibility of re-refinement of used products that contain chlorine, since chlorine acts a catalytic poison. If this products are burned, incomplete combustion also forms hydrochloric acid, which comes in environmentally round cycle and leads to increased environmental pollution. [3]

3. EXPERIMENTAL PART

Because of all findings on harmfulness of chlorparaffins, new components are being researched, which might be more ecologically acceptable, with function to serve as a replacement for chlorparaffins in all places where severe metalworking operations are, and where it was, until recent, only EP additive.

A new generation of EP additives has been developed, that are, by their chemistry, compounds of sulphur and phosphorus, and new generation of synthetic esters is currently being tested in severe metalworking fluids. A special focus is on synergism of synthetic esters and sulphur based additives.

For research of antiwear and EP characteristics of formulations that have chlorparaffin replaced with two synthetic esters, we chose formulations

for vertical broaching, drawing and final finishing operations, like fine stamping.

Characteristics of synthetic ester that were used in tested formulations are listed in Table 1. In Table 2. are listed characteristics and methods used for metalworking samples testing for all three metalworking operations. [4]

Table 1. Characteristics of syn ester 1 i 2.

| Characteristic | Syn ester 1 | Syn ester 2 |
|----------------------------|-------------------|----------------------------|
| Appearance | Hazy. Light amber | Slightly hazy. Light amber |
| Specific gravity @ 25 °C | 1,00 | 1,01 |
| Acid number, mg KOH/g | 20 | <5 |
| Viscosity (cSt) at 100 °C | 244 | 883 |
| Viscosity index | 203 | 267 |
| Iodine value | <2 | <5 |
| Molecular Weight (approx.) | 25 000 | 160 000 |

Table 2. Characteristics and testing methods.

| Characteristic | Method | Unit |
|--------------------|----------------|--------------------|
| Viscosity at 40 °C | BAS ISO 3104 | mm ² /s |
| Acid number | ISO 6618 | mg KOH/g |
| Cu corrosion | ASTM D 130 | - |
| Wear | ASTM D 2266-01 | mm |
| Welding point | ASTM D 2596-98 | N |

Table 3. Testing results of samples for vertical broaching operations that contain chlorparaffine.

| Neat oil for vertical broaching | | | | |
|------------------------------------|-------|-------|-------|-------------|
| Sample | 1 | 2 | 3 | 4 |
| Chlorinated paraffine, %m/m | - | 10 | 20 | 30 |
| Additive A, m/m | 4 | 4 | 4 | 4 |
| Base oil, % m/m | 96 | 86 | 76 | 66 |
| Results | | | | |
| | 1 | 2 | 3 | 4 |
| Wear, 40 kg, mm | 0,97 | 0,84 | 0,89 | 1,08 |
| Welding point, N | 4200 | 3000 | 5500 | 7000 |
| V at 40 °C, mm ² /s | 23,14 | 29,58 | 35,12 | 37,22 |
| Cu corrosion | 4a | 4a | 4a | 4a |
| Acid number, mg KOH/gr | 0,86 | 0,82 | 0,83 | 0,80 |

As a replacement for chlorparaffin for broaching operations, syn ester 1 was chosen, that was used to prepare samples with ester concentration of 2, 6 and 10 % (Table 4). Because increased concentration of syn ester 1 didn't lead to increased welding point (Figure 3) which was a goal for this research, we gave up from further research of using this syn ester type for these kinds of broaching. Formulation of these samples contained additives based of active sulphur, but beside lower diameter of wear in wear test, welding points remained much lower than with samples that had chlorparaffin. Testing results of samples for broaching operations that contain chlorparaffin are listed in Table 3, and ones containing syn ester are in Table 4.

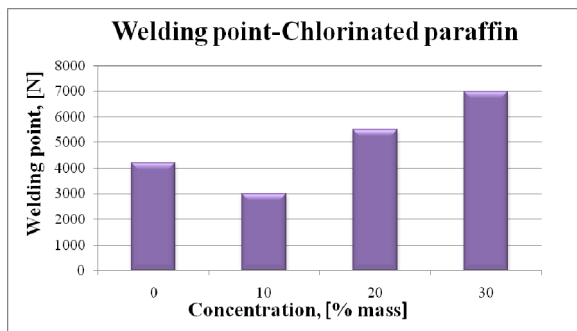


Figure 1. Test results for samples of welding points for vertical broaching operations with different concentrations of chlorparaffine.

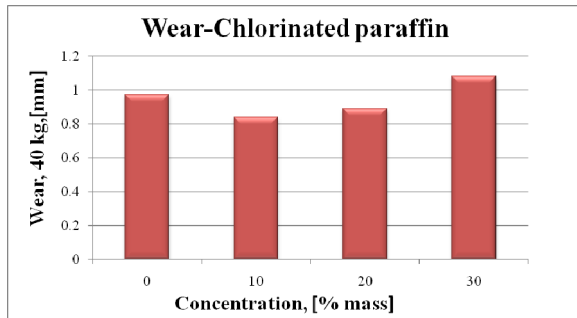


Figure 2. Test results for samples of wear scar for vertical broaching operations with different concentrations of chlorparaffine.

In Figure 1 are shown welding point values in comparison to increase of chlorparaffins content, were broaching operation require chlorparaffins content of up to 30% in order to achieve welding point of 7000 N, which will provide good processing.

In Figure 2 are shown wear diameter values compared to chlorparaffin content. Diameter wear test values in broaching operations are not so important, welding point values.

Table 4. Test results of samples for vertical broaching operations which formulation contains Syn ester 1.

| Neat oil for vertical broaching | | | | |
|---------------------------------|-------|-------|-------------|-------------|
| Sample | 1 | 2 | 3 | 4 |
| Syn ester 1 % m/m | - | 2 | 6 | 10 |
| Additive A, % m/m | 4 | 4 | 4 | 4 |
| Base oil, % m/m | 96 | 94 | 90 | 86 |
| Results | | | | |
| | 1 | 2 | 3 | 4 |
| Wear, 40 kg, mm | 0,96 | 0,76 | 0,61 | 0,67 |
| Welding point, N | 3800 | 4000 | 4800 | 4800 |
| V at 40 °C, mm ² /s | 34,47 | 29,85 | 31,58 | 37,83 |
| Cu corrosion | 4c | 3b | 3a | 3b |
| Acid number | 0,81 | 1,85 | 3,95 | 6,21 |

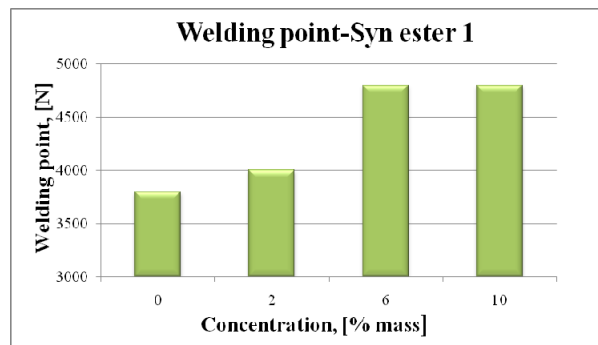


Figure 3. Test results for samples of welding points for vertical broaching operations with different concentrations of Syn ester 1.

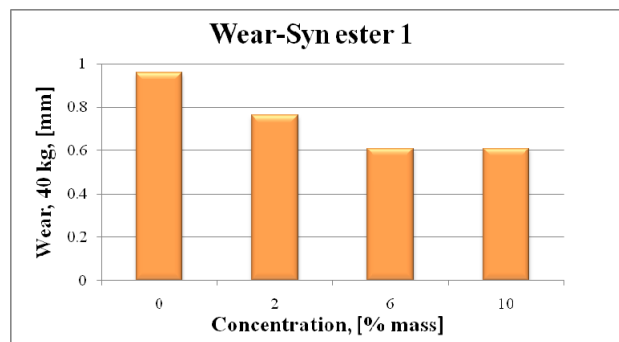


Figure 4. Test results for samples of wear scar for vertical broaching operations with different concentrations of Syn ester 1.

With Syn ester 1 are prepared samples for fine stamping operations, whose test results are compared with the classical formulations containing optimal concentration of chlorinated paraffine to meet the performance which this operation demands. Test results of welding points (Table 5. and Figure. 5.) shows that nor with the maximal concentration of Syn ester 1 do not achieve satisfactory results. Because of that, samples with Syn ester 2 are prepared where test results of welding point has shown that nor with it do not achieve the result which in practical conditions could meet all expected performance. (Table 6. and Figure 7.)

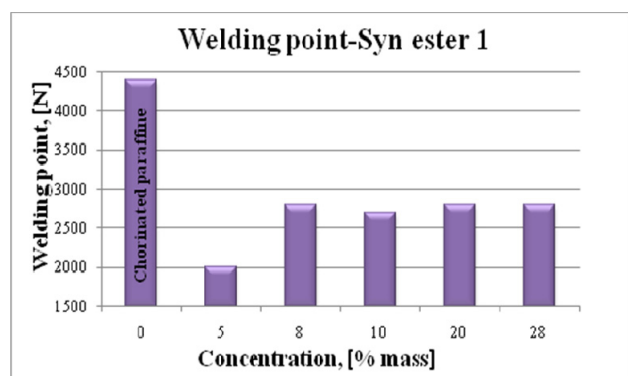


Figure 5. Test results for samples of welding points for fine stamping operations with different concentrations of Syn ester 1 and classical formulation with chlorparaffine.

Table 5. Test results of samples for fine stamping operation whose formulation contains chlorparaffine (Sample 1) and Syn ester 1 (2-6).

| Neat oil for stamping | | | | | | |
|---------------------------|-------------|------|------|-------|------|-------|
| Sample | 1 | 2 | 3 | 4 | 5 | 6 |
| Syn ester 1, % m/m | - | 5 | 8 | 10 | 20 | 28 |
| Hlorparafin | 28 | - | - | - | - | - |
| Additive package, % m/m | 4 | 2 | 2 | 2 | 2 | 2 |
| Base oil, % m/m | 68 | 93 | 90 | 88 | 78 | 70 |
| Results | | | | | | |
| | 1 | 2 | 3 | 4 | 5 | 6 |
| Wear, 40 kg, mm | 0,71 | 0,42 | 0,40 | 0,42 | 0,41 | 0,41 |
| Welding point, N | 4400 | 2000 | 280 | 2700 | 2800 | 2800 |
| V at 40 °C | 89,2 | 74,8 | 85,2 | 89,38 | 97,7 | 106,5 |
| Cu corrosion | 1a | 1a | 1a | 3a | 1a | 3a |
| Acid number | 1,46 | 5,35 | 6,62 | 7,90 | 13,4 | 18,16 |

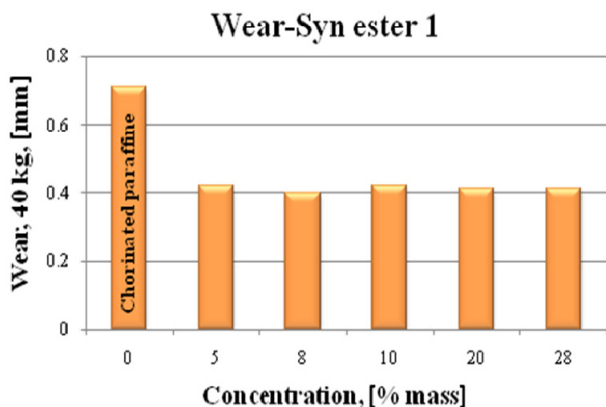


Figure 6. Test results of wear diameter with samples for stamping operations with different concentrations of Syn ester 1.

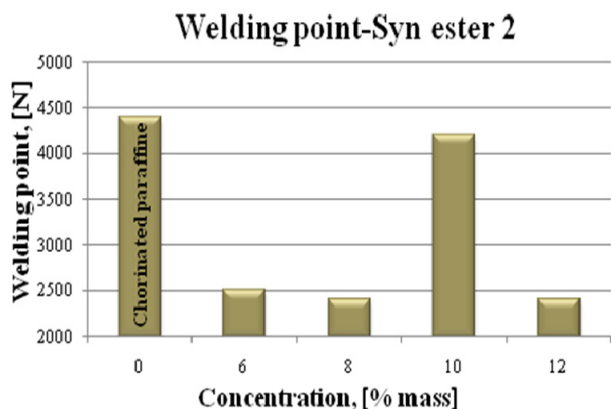


Figure 7. Test results of welding points with samples for stamping operations with different concentrations of Syn ester 2 and classical formulation with chlorparaffine.

For steel profile drawing operations there is formulation with the optimal amount of chlorparaffins and additive packages, which

completely satisfies all performance demands for that operation. With Syn ester 2 optimal quantity of additive package there is a formulation whose test welding results are close to those with chlorparaffin. (Table 7. and Figure 9.)

Table 6. Test results of samples for fine stamping operation whose formulation contains chlorparaffine (Sample 1) and Syn ester 2 (2-5).

| Neat oil for stamping | | | | | |
|--------------------------------|------|-------|-------|-------|-------|
| Sample | 1 | 2 | 3 | 4 | 5 |
| Syn ester 2, % m/m | - | 6 | 8 | 10 | 12 |
| Hlorparafin | 28 | - | - | - | - |
| Additive package, % m/m | 4 | 2 | 2 | 2 | 2 |
| Base oil, % m/m | 68 | 92 | 90 | 88 | 86 |
| Results | | | | | |
| | 1 | 2 | 3 | 4 | 5 |
| Wear, 40 kg, mm | 0,71 | 0,45 | 0,47 | 0,5 | 0,45 |
| Welding point, N | 4400 | 2500 | 2400 | 4200 | 2400 |
| V at 40 °C, mm ² /s | 89,1 | 89,91 | 95,36 | 96,33 | 98,99 |
| Cu corrosion (3 h, 100 °C) | 1 a | 1a | 1a | 1a | 1a |
| Acid number | 1,46 | 4,45 | 5,06 | 5,69 | 6,35 |

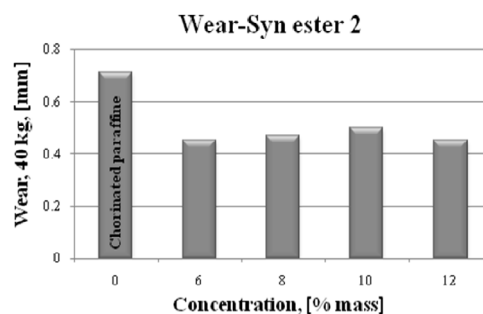
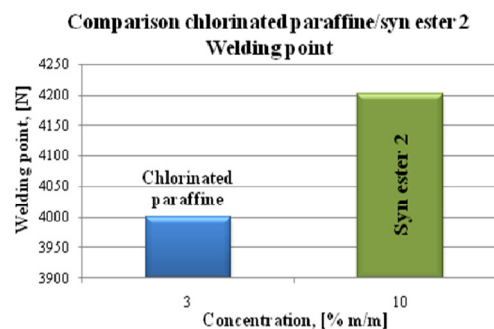


Figure 8. Test results of wear diameter with for stamping operations with different concentrations of Syn ester 2 and classical formulation with chlorparaffine.



Slika 9. Test results of welding points with samples for drawing operations with classical formulation with chlorparaffine and Syn ester 2.

Table 7. Test results of oil samples for drawing operations with classical formulation with chlorinated paraffine and Syn ester 2.

| Neat oil for drawing | | | |
|--------------------------------|-------|-------------------------------|-------|
| Sample | 1 | Sample | 2 |
| Chlorinated paraffine, % m/m | 3 | Syn ester 2, % m/m | 10 |
| Additive package, % m/m | 18 | Additive package, % m/m | 7 |
| Base oil, % m/m | 56 | Base oil, % m/m | 73 |
| Vegetable oil, % m/m | 23 | Vegetable oil, % m/m | 10 |
| Results | | | |
| | 1 | | 2 |
| Wear, 40 kg, mm | 0,44 | Wear, 40 kg,mm | 0,35 |
| Welding point, N | 4000 | Welding point,N | 4200 |
| V at 40 °C, mm ² /s | 44,26 | Vat 40 °C, mm ² /s | 40,02 |
| Cu corrosion (3 h, 100 °C) | 3a | Cu corrosion (3 h, 100 °C) | 1b |
| Acid number, mg KOH/gr | 4,67 | Acid number, mg KOH/gr | 7,81 |

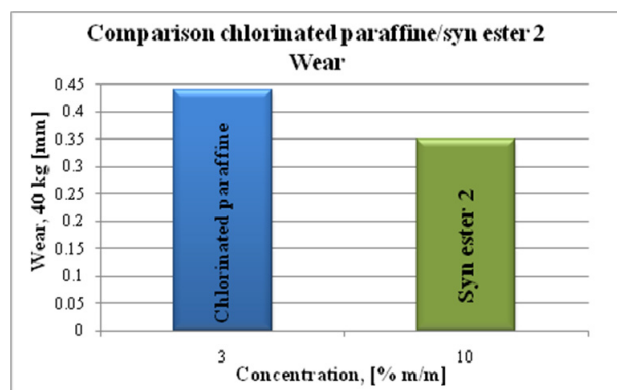


Figure 10. Test results of diameter wear with samples for drawing operations with classical formulation with chlorparaffine and Syn ester 2.

4. CONCLUSION

Test results of samples of neat oils intended for operations: broaching, fine stamping and drawing

which are prepared with Syn esters, as a replacement for chlorinated paraffine, shows:

- test result of welding points has showed that at heavy operations such as a broaching with Syn ester 1 they do not achieve good results, although it is attempted to use synergistic effect of esters and additives with active sulphur.

- with stamping operations, which is also considered as heavy, welding points test showed that with two different formulated Syn estes it is impossible to achieve good results, which will also affect application conditions

- based on test results for steel profiles drawing operations, one can conclude that Syn ester 2 can be used for formulations intended for that operations, with reduced quantities of other additives.

This is the start of one comprehensive research, in laboratory and application conditions, that are being done with additive manufacturers. Test results shows that it is hard to achieve replacement for chlorparaffins in formulations of heavy metalworking operations, like broaching, deep drilling, stamping and others.

Constant arguing about usage of chlorparaffins and their allowed chain length, confuse both users and manufacturers. But it initiated many studies regarding that problematic and efforts to find adequate replacement for chlorparaffins, as soon as possible.

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