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RESEARCH

Possibility of Replacing the Chorinated Paraffins in Metalworking Fluids

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A B S T R A C T

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 this addition, 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.

1. INTRODUCTION

Lubricants are vital components in transportation, as with most of industrial equipment. A proper selection of the lubricant and lubricating methods increase the lifetime of machinery and decrease operation and maintenance costs. These effects manifest themselves in a decrease of energy consumption, lower working temperatures and shorter down times.

Effectiveness of lubricants depends on numerous interrelated factors that are determining the influence of a lubricant on friction and wear of the vital machine parts and equipment. They include the properties of lubricants and changes that occur in the properties during exploitation, characteristics of frictional surfaces, character of interactions of the lubricant components and surface material, speed, load, temperature and other parameters of the working regime. [1]

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 characterisics 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, antifriction 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. [2]

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 lubricanst, 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
- Planing (during operation it is identical to scraping, but the process is discontinuous)
- Drilling (beveling, widely considered: drilling, widening, reaming)

- Miling (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. Forging is also one of the demanding operations. Main factors that influence tribological characteristics are classified as:

- Geometric factors
- Kinematic factors
- Dynamic factors
- Physical-chemical factors and
- Energy factors

The factors 1 and 4 define basic properties of the contact pairs, while the others define basic parameters of the friction process. [3]

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

Lubricants operate in the boundary between moving metal parts to prevent the contact that could lead to an increase in friction, increase in wear and eventually welding. The classic type of component used to prevent these phenomena is a boundary lubricity additive. The boundary lubricity additive typically functions by adsorbing on the metal surface to form a film that will reduce metal-to-metal contact. This function is achieved because the boundary lubricity additive has a polar head group that can interact with the metal surface and a tail group that is compatible with the lubricant carrier (mineral oil, synthetic basestock or water).

STLE member Frank Kroto, global technology manager for The Lubrizol Corp. says, "EP additive use is formulation and application dependent. For severe metal removal applications such as tapping, reaming and broaching and metal forming operations, EP additives provide the needed performance features to minimize metal-to-metal contact and improve tool life. [2]

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 ^{0}C, phosphorus are activated at higher temperatures and sulphur at even higher temperature range which ends at 1000 ^{0}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 ^{o}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 suphur 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 cancallation 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 unstability 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 the most popular and widely used extreme pressure lubricant additives in metalworking fluid formulations. They offer numerous advantages: versatility for use in both oil and water-based formulations; ease of formulation; activity in a wide range of temperatures and conditions; lightness of color and cost efficiency. [4]

Chloroparaffins (CPs, also called polychlorinated n-alkanes) are complex mixtures of n-alkane homologues with carbon chain lengths between C10 and C30 and a chlorination degree between 30 % and 70 %. CPs are colourless to intense yellowish, low to highly oily liquids or glassy to waxy solids boiling over 200 °C with the release of hydrogen chloride. They are insoluble in water but dissolve in most non-polar organic solvents. Their viscosities and densities increase with increasing chlorine content of a given carbon chain length. However, volatility decreases with increasing chain length and degree of chlorination . CPs are mainly used as extreme pressure and temperature additives in metal working, as plasticizer in paints, as additives to adhesives and sealants and as flame retardants in rubber and polymeric materials. [5]

Chlorinated paraffines are divided in three classes based on the chain lenght:

- Short-chain, C_{10-13}
- Medium-chain, C_{14-17}
- Long-chain, C_{18-30}

The most commonly used chlorinated paraffins were with 35-70 % of chlorine and with the hydrocarbon base with C_{10-20}.

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.[6]

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 rerafination of used products that contain chlorine, since chlorine acts a catalityc poison. If this products are burned, incomplete combustion also forms hydrochloric acid, which comes in environmentally round cycle and leads to increased environmental pollution. [7]

Until late in the second half of the 20th century the following equation could be applied:

Increase in Performance =
Increase of Toxicological Problems

Due to different factors today this equation has become invalid.

- By modern refining technologies mineral oils can be freed from their toxic substances.
- For the development of new additives the toxicological parameters have become a major subject.
- Triggered by local or global oilshortages the development of synthetic base oils (PAOs, p polyglycols, siliconoils, esters) has been granted high priority status. These base are contrary to mineral oils not a multi-product-mix. Their toxic characteristics are more uniform and–in most cases- also less critical.

All of the before mentioned facts resulted in the development to of a new generation of high-performance lubricants which can best be described with the following summary:

Increase in Performance
PLUS!
Decrease of Toxicological Problems [8]

3. EXPERIMENTAL PART

There are two primary market forces for eliminating or substantially reducing the chlorine content in metalworking fluids: health and safety issues related to chlorinated materials and disposal of metalworking fluids which contain halogens.

Among these two main reasons, another suitable reason for eliminating chlorine-containing compound from the fluid is that chloride ion is generated when clorinated compound reacts with metal surface. Chlorides are quite corrosive at fairly low concentration, often requiring supplemental corrosion inhibitors be added to the system. [9]

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 opperations 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.

Higher molecular weight polymerized esters display superior thermal and oxidative stability compared to other types of esters. This characteristic coupled with their higher viscosity gradient enables polymeric esters to maintain a film on the metal surface at higher temperatures. [2]

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. [10]

Syn ester 1 is a high molecular weight polymerized ester. By its composition it represents a pentaerythritol initiated polymer of a mixture of monobasic acids (i.e., stearic acid and coconut fatty acids) and a dibasic acid (i.e., adipic acid).

Syn ester 2 is a high molecular weight polymerized ester that is a pentaerythritol initiated polymer of a mixture of a monobasic acid (i.e., coconut fatty acids) and a dibasic acid (i.e., adipic acid). [10]

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 ^{0}C	1,00	1,01
Acid number, mg KOH/g	20	<5
Viscosity (cSt) at 100 ^{0}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 ^{0}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

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 (Fig. 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 (Fig. 4). 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.

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 ^{0}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

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 ^{0}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

In Fig. 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.

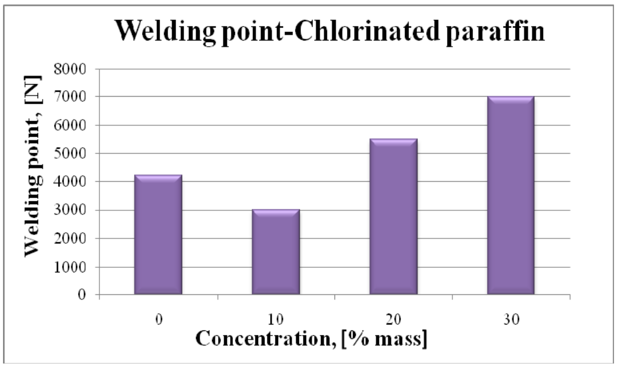

Fig. 1. Test results for samples of welding points for vertical broaching operations with different concentrations of chlorparaffine.

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

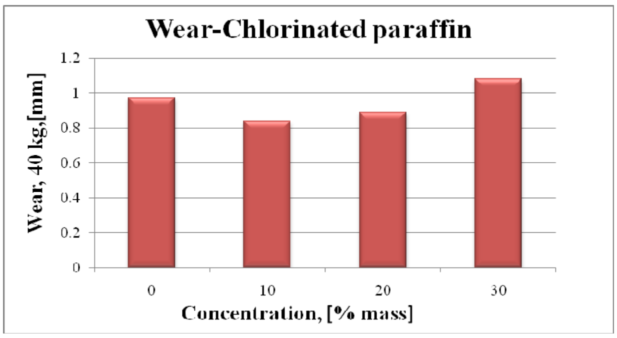

Fig. 2. Test results for samples of wear scar for vertical broaching operations with different concentrations of chlorparaffine.

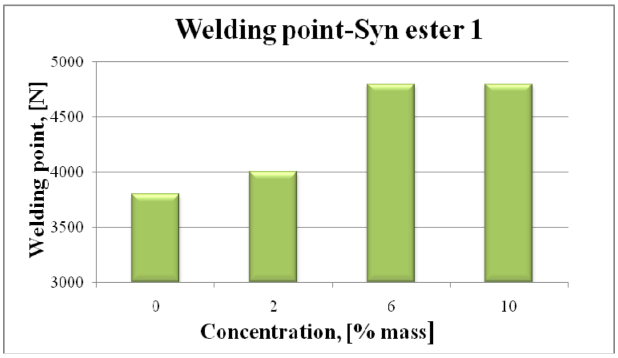

Fig. 3. Test results for samples of welding points for vertical broaching operations with different concentrations of Syn ester 1.

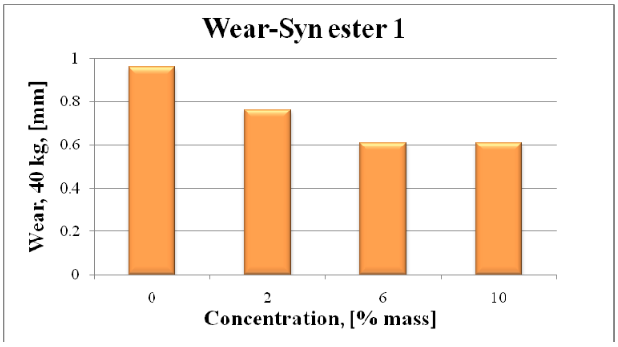

Fig. 4. Test results for samples of wear scar for vertical broaching operations with different concentrations of Syn ester 1.

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 Fig.. 5.) shows that nor with the maximal concentration of Syn ester 1 do not achieve satisfactory results.

Table 5. Test results of samples for fine stamping operation whose forrmulation 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 ^{0}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

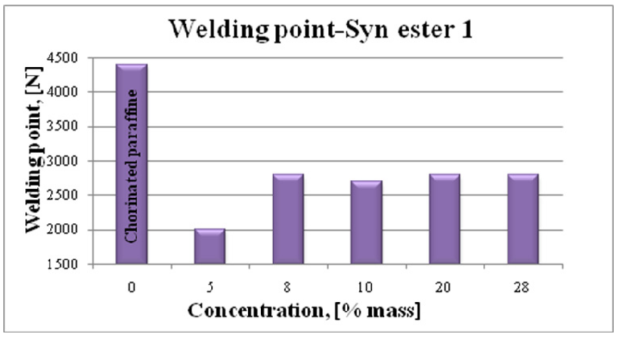

Fig. 5. Test results for samples of welding points for fine stamping operations with different concentrations of Syn ester 1 and classical formulation with chlorparaffine.

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 Fig. 7).

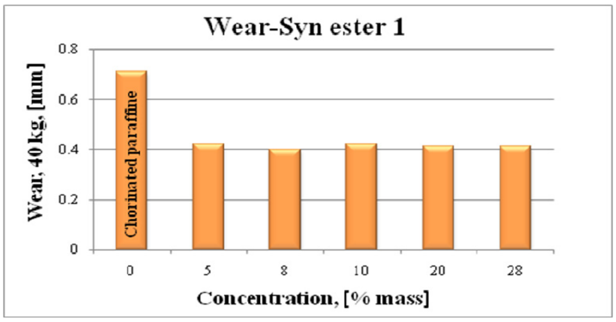

Fig. 6. Test results of wear diametar with samples for stamping operations with different concentrations of Syn ester 1.

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

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 ^{0}C, mm^2/s	44,26	Vat 40 ^{0}C, mm^2/s	40,02
Cu corrosion (3 h, 100 ^{0}C)	3a	Cu corrosion (3 h, 100 ^{0}C)	1b
Acid number, mg KOH/gr	4,67	Acid number, mg KOH/gr	7,81

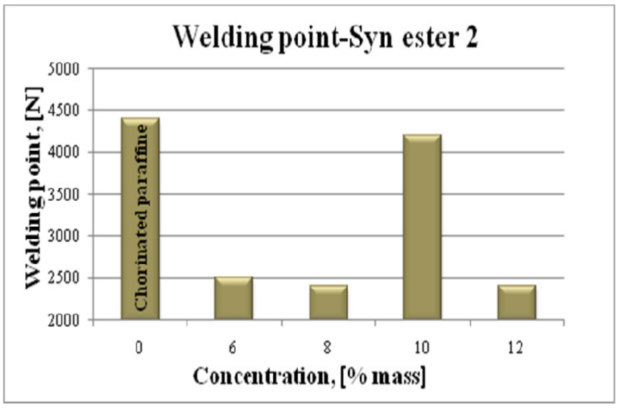

Fig. 7. Test results of welding points with samples for stamping operations with different concentrations of Syn ester 2 and classical formulation with chlorparaffine.

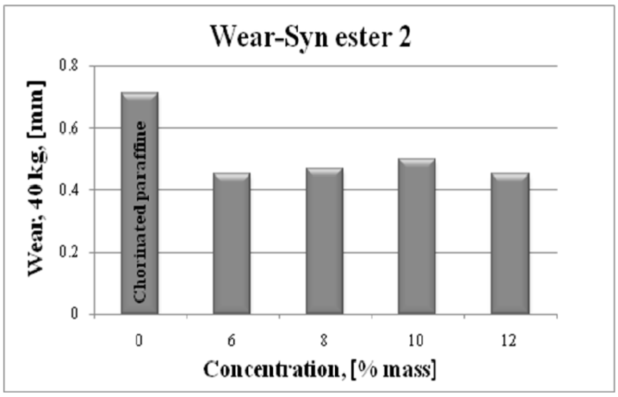

Fig. 8. Test results of wear diametar with for stamping operations with different concentrations of Syn ester 2 and classical formulation with chlorparaffine.

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

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 ^{0}C, mm^2/s	89,1	89,91	95,36	96,33	98,99
Cu corrosion (3 h, 100 ^{0}C)	1 a	1a	1a	1a	1a
Acid number	1,46	4,45	5,06	5,69	6,35

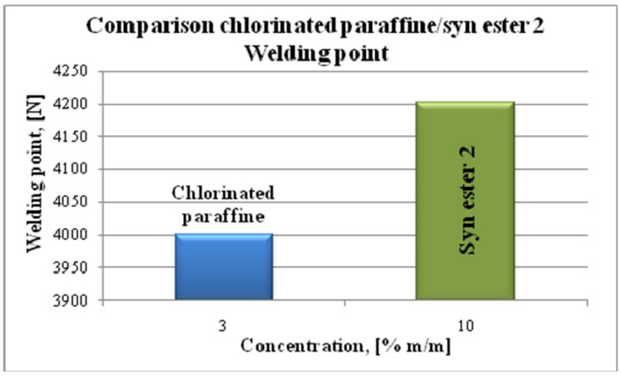

Fig. 9. Test results of welding points with samples for drawing operations with classical formulation with chlorparaffine and Syn ester 2.

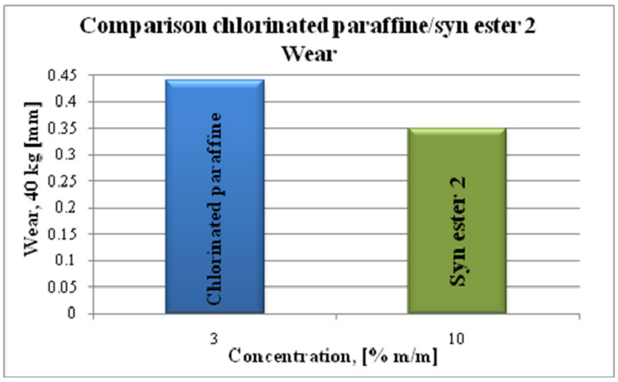

Fig. 10. Test results of diameter wear with samples for drawing operations with classical formulation with chlorparaffine and Syn ester 2.

For steel profile drawing operations there is formulation with the optimal amount of chlorparaffins and additive packages, which completly satisfies all performance demands for that operation. With Syn estre 2 optimal quantity of additive package there is a formulation whose test welding results are close to those with chlorparaffin (Table 7. i Fig. 9.).

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 estres 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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