INFLUENCE OF ORGANIC ADDITIVES IN HYDROCARBON BASED DIELECTRIC FLUIDS FOR SPARK EROSION

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ABSTRACT

Studies at the Otto-von-Guericke-University of Magdeburg in cooperation with oelheld GmbH in Stuttgart have analyzed the influence of organic molecules with polar or non-polar characteristics on the breakdown phases of the plasma channel of the dielectric working fluid. The influence of the different additive molecules on the formation of the Helmholtz-Layer and on the ignition and discharge mechanism in dependency of the ignition peak of the pulse current will be discussed. For instance polar additives of short molecular size reinforce the influence of the double layer onto the pre-igniting mechanism, so that in spite of unchanged insulating characteristics the ignition voltage and ignition delay time are reduced.

KEYWORDS: Dielectric liquids, dielectric breakdown, electro discharge machining, additives

1. INTRODUCTION

Spark erosion is a process of machining of very hard materials and parts even with very complicated geometry. It is based on the effect of electrical discharges in a dielectric working fluid in which small craters are produced on the surface of the work piece.
The essential tasks of the working fluid are:

- transportation of the removed particles
- intensification of the energy density in the plasma channel
- reconditioning of the dielectric strength
- cooling of the electrodes
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The pre-ignition and breakdown behaviour in spark erosion processes are determined by a large number of different influences, especially by the chemical and physical properties of the dielectric working fluid. This report shows the specific influences of molecules with a defined chemical structure, which were dissolved in a hydrocarbon based dielectric fluid.

The investigations are not only interesting for achieving an improvement of technological parameters like productivity, wear or surface roughness in industrial practise. They are even more necessary for a better understanding of the physical and chemical mechanism through which the EDM process is influenced by the dielectric fluid.

2. EXPERIMENTAL METHODS

The analysis of the influences of the dielectric working fluids with different additives was carried out by the investigation of single pulse discharges. For the electrical characteristics of these single pulses a measuring system consisting of a measuring cell, a process energy source, a guidance and positioning system and an electrical measuring system for current and voltage courses were developed [1], [2].

An electrode arrangement for creating the discharge is carried out as peak-to-peak geometry. Reproducible gap conditions (flow conditions) can be established with the aid of a pump.

3. WORKING FLUID AND ADDITIVES

For sinking EDM usually saturated aliphatic hydrocarbons are applied. Compared with deionised water, the use of hydrocarbons has the advantage of a lower surface roughness and a smaller heat affected zone at the machined work piece. n-Dodecane, a saturated aliphatic hydrocarbon compound with a non branched chain of 12 carbon atoms, was used as a basic working fluid for the tests. This dielectric liquid corresponds in its physical and chemical properties to commonly used dielectric fluids in EDM but has better defined properties. n-Dodecane consists of carbon and hydrogen atoms which are connected by single covalent bonds. Because of the weak polarity of the bondings and their symmetric structure, all alkanes are practically non-polar and they are not able to arrange themselves in an electrical field. In a previous testing series hydrocarbon, molecules with cyclic aliphatic as well as aromatic structures were added to the n-dodecane. This first testing series includes benzene, toluene, fluorobenzene, cyclohexane and cyclohexanone in a concentration of 2 mol/L in n-dodecane [3].

Within these tests, the benzene and the fluorobenzene clearly show the best ignition behaviour at single discharges as they need an average voltage between 200 and 300 V for ignition. The toluene needs a slightly increased ignition voltage in comparison with the pure n-dodecane. Both cyclic aliphatic additives, the cyclohexane as well as the cyclohexanone need higher ignition voltages. In ignition and breakdown, behaviour there seems to be no difference between these two compounds.

A new testing series were conducted to develop a thesis of the effect of the additives on the pre-ignition and breakdown process. Within these series the ignition voltages and currents, the spark burning voltage and the ignition delay time were analysed. The additionally tested substances were the aromatic compounds biphenyl, 2-chloronaphthalene and cycloocta-tetraene. As testing parameters, a gap width between 5 and 20 µm and a pulse duration of 20 µs were used. The current of the energy source (pulse current) was varied between 5 …25 A.

Because of its conjugated carbon double bonds aromatic compounds show sp^2-hybridisated molecule orbitals. The remaining p-orbitals of the hydrocarbons overlap above and below the plane of the ring shaped molecule and form de-located π-bonds. The π-electron density lies in doughnut-shaped regions both above and below the plane of the ring. These clouds of π-electrons could easily be influenced and polarized by an electrical potential difference. This led to their ability to arrange in an electrical field, which may be helpful for improving the ignition behaviour of dielectric working fluids.

3.1 Benzene 0.5 mol/L

When testing the benzene with a concentration of 0.5 mol/L in n-dodecane a dependency between the electrode gap width and the values ignition voltage and ignition peak of the pulse current as well as the ignition delay time were observed:

Table 1 Average measured values of benzene 0.5 mol/L

Gap width [µm]	Ignition voltage [V]	Spark burning voltage [V]	Ignition peak of pulse cur-rent [A]	Ignition delay time [µs]
5 A – pulse current				
5	310	29 – 35	7.9	0.04
10	358	28 – 32	13.1	0.47
20	358	29 - 36	12.5	0.41
25 A – pulse current				
5	330	31 – 38	34.6	0.04
10	332	30 – 36	35.8	0.06
20	358	31 - 37	37.6	0.09

With an increase of the distance of the electrodes from 5 to 10 µm these values rose clearly. A further widening of the gap had no clear effect. In Figure 1 a typical course of voltage and current within an electrical discharge is displayed. The gap width was 10 µm, pulse duration 20 µs and the pulse burning current 5A. The ignition delay at the beginning of the pulse is clearly visible. At higher current the increase of ignition time and ignition peak of the pulse current at higher gap widths was much lower than at 5 A.

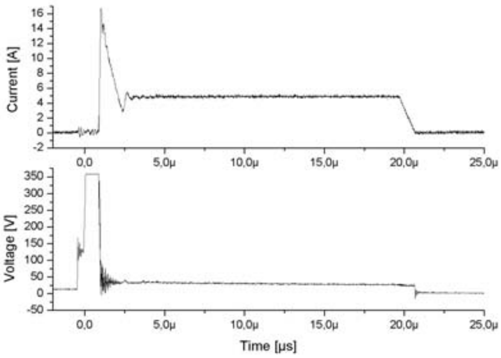

Figure 1: Voltage and current course (5A) for 0.5 mol/L benzene at a gap width of 10

3.2 Biphenyl 0.5 mol/L

The biphenyl molecule is non-polar and has the structure of two benzene rings, linked by a single bond. Due to its conjugated carbon double bonds a charge can be distributed over the complete molecule. This means an additional stabilization of charges in comparison with the benzene molecule.

When using the biphenyl as an additive with a concentration of 0.5 mol/L in n-dodecane, in comparison to benzene there was also a strong decrease of the ignition peak of the pulse current and the ignition delay time observed at the gap width of 10 µm. With further increased gap width, the ignition peak of the pulse current and the delay time increased strongly (Table 2).

Table 2 Average measured values of biphenyl 0.5 mol/L

Gap width [µm]	Ignition voltage [V]	Spark burning voltage [V]	Ignition peak of pulse cur-rent [A]	Ignition delay time [µs]
5 A – pulse current				
5	327	27 – 34	8.7	0.04
10	346	28 – 32	8.1	0.05
20	358	28 - 35	14.5	1.46
25 A – pulse current				
5	344	30 – 35	34.8	0.04
10	342	30 – 36	38.4	0.09
20	358	31 - 37	42.3	1.41

When testing the biphenyl with a concentration of 0.5 mol/L in n-dodecane with a pulse current of 25 A, the values of ignition voltage and ignition delay time are nearly the same than at 5 A.

There is nearly no influence of pulse current or pulse energy to be seen on these values. A typical course of voltage and current at a gap width of 10 µm is displayed in Figure 3. At gap widths of 5 and 10 µm the ignition delay time at 5 A as well as 25 A is much shorter and the ignition peak of the pulse current is clearly lower than for the benzene.

Furthermore the ignition voltage is significantly lower (Figure 2). By a gap width of 20 µm, the ignition peak of the pulse current and the delay time increased to the highest values of these testing series.

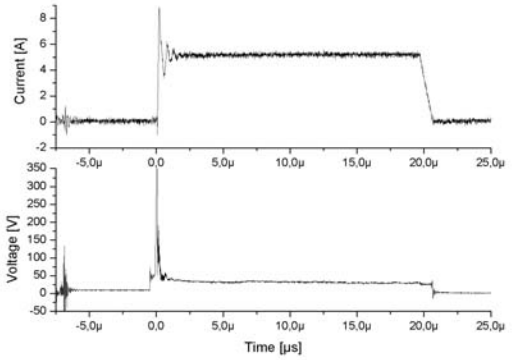

Figure 2: Course of voltage and current at 5 A for 0.5 mol/L biphenyl at a gap width of 10 µm

3.3 2-Chloronaphthalene

2-Chloronaphthalene consists of two condensed benzene rings with a chlorine atom added at one ring. Due to the high electronegativity of the chlorine atom the molecule has a high polarity. Over the complete range of electrode distances, the addition of 2-chloronaphthalene has shown low values for ignition voltage, ignition peak of pulse current and ignition delay time. The values measured at 20 µm gap width were the lowest of the complete testing series (Table 3). At 25 A there is only a slight influence of the gap width on ignition peak of pulse current and on the ignition delay time to be seen. At a gap width of 20 µm the deviation from the mean value was increased, the process seemed to be less stable. Also the graphs of the current and voltage courses show the very even process of the ignitions (Figure 3).

Table 3 Average measured values of 2-chloronaphthalene 0.5 mol/L

Gap width [µm]	Ignition voltage [V]	Spark burning voltage [V]	Ignition peak of pulse cur-rent [A]	Ignition delay time [µs]
5 A – pulse current				
5	308	27 – 34	7.7	0.03
10	348	29 – 36	8.4	0.06
20	342	28 - 34	10.7	0.17
25 A – pulse current				
5	287	31 – 36	35.4	0.02
10	317	29 – 35	35.6	0.04
20	358	30 - 35	35.9	0.04

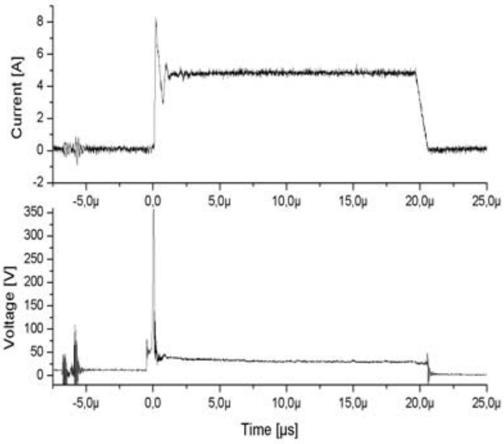

Figure 3: Course of voltage and current at 5 A for 0.5 mol/L2-chloronaphthalene at a gap width of 10 µm

3.4 Cyclooctatetraene 0.5 mol/L

The cyclooctatetraene molecule also has an aromatic structure. In contrast to benzene and its derivatives it is able to absorb two electrons. With the spark burning current of 5 A and also 25 A and the pulse duration of 20 µs it was only possible to make the measurements with a gap width of 5 µm. The values for ignition peak of pulse current and for ignition delay time at this gap width are clearly higher than at all other tested additives (Table 4).

Table 4: Average measured values of cycloocta-tetraene 0.5 mol/L

Gap width [µm]	Ignition voltage [V]	Spark burning voltage [V]	Ignition peak of pulse cur-rent [A]	Ignition delay time [µs]
5 A – pulse current				
5	358	27 - 32	12.8	2.18
25 A – pulse current				
5	348	28 – 34	24.9	0.24

For 5 A there were also a wide deviation of the measured values observed. With both pulse currents it was not possible to cause an ignition at higher gap widths. Figure 4 shows an extreme example for the ignition delay at the voltage and current courses of 0.5 mol/L cyclooctatetraene at 5A.

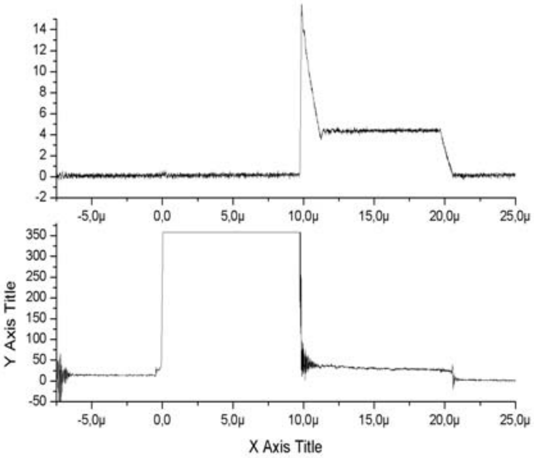

Figure 4: Course of voltage and current at 5 A for 0.5 mol/L cyclooctatetraene at a gap width of 5 µm

4. THESIS OF THE EFFECTS

To explain the measured effects, different models have been developed and checked for their applicability for the EDM process.

4.1 Influence on double layers

Following the Helmholtz and Gouy-Chapman-Stern models an interchange of charges through the phase boundary occurs from the beginning of a contact between metal electrodes and dielectric base fluid. On both sides of this phase boundary electrochemical double layers are formed (Figure 5).

On the side of the metal the electrons are towering over the positive charged ion hulls, the dipole layer towers with its negative side into the liquid and is forming the inner Helmholtz plane.

An outer Helmholtz plane can be formed on the liquid side of the phase boundary by polar molecules or positive charge carriers. Both monomolecular layers together form the compact layer. Outside the compact layer there is the so called diffuse layer, a region also consisting of positive ions and polarized molecules which are not rigidly held but tend to diffuse into the liquid.

The thickness of this layer is dependant on the size of the molecules and also on their ability to be polarized by an electrical field.

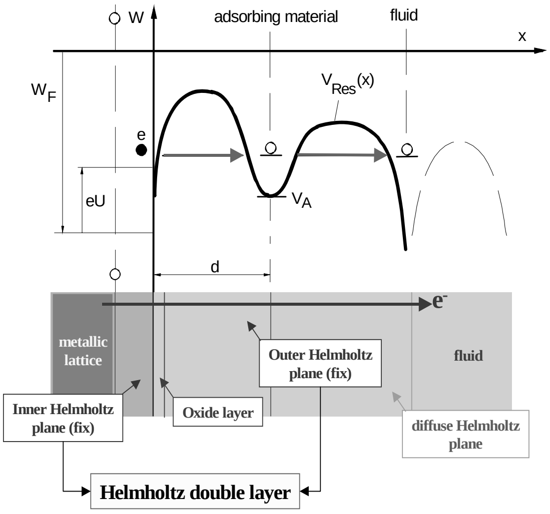

Figure 5: Formation of the Helmholtz double layers

The aromatic molecules, polar or polarized by an electrical field are influencing the effective gap width between the electrodes. For an adjusted gap width of 5 µm the benzene molecules show a reduction of the electrical resistance and delay time. For a gap width of 10 µm this effect can only be seen by using the biphenyl which has a much higher molecular size (Table 5).

Table 5: Molecular size and ionisation potentials of the tested substances

Substance	Approx. max. length (diameter) [pm]	Ionization potentials [eV]
n-Dodecane	1627	10,10
Benzene	738	9,25
Biphenyl	1627	8,30
2-Chloro-naphthalene	1180	8,10
Cyclooctatetra-ene	1125	n.d.

The presence and structure of the outer and the diffuse Helmholtz layers are also depending on the dipole character or the ability of the molecules of being polarized in an electrical field. The n-dodecane molecule is non-polar. Without an outer electrical field it doesn’t arrange itself between the metal plates of the electrodes.

There are no outer and diffuse Helmholtz layers. When influenced by a strong electrical field a weak polarization may occur which leads to the formation of amorphous Helmholtz layers.

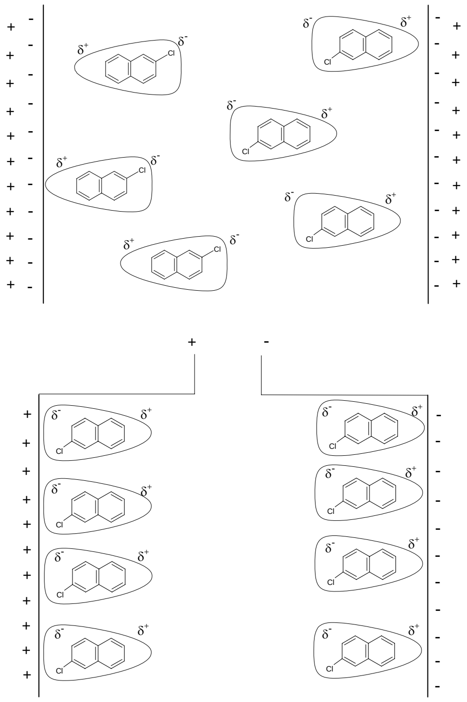

Figure 6: Arrangement of the 2-chloro-naphthalene molecules between metal plates without an electrical field (a) and under the influence of an electrical field (b)

Polar molecules like 2-chloronaphthalene are able to arrange themselves to metal surfaces even without the presence of an electrical field. Under the influence of an electrical field they will form close Helmholtz layers with a high concentration of molecules in it (Figure 6a+b). Because of the high concentration of molecules with a comparably high length and a clear orientation to the electrode surface these layers have a strong influence on the pre-ignition and breakdown behaviour even at gap widths of 20 µm. Especially for those molecules which are dipoles or which can be polarized in the electrical field, the probability density in the compact and diffuse layers is much higher than for the almost non-polar n-dodecane molecules. By increasing the pulse current 5 times to 25 A, which results in an 25 times increase of the pulse energy, the ignition peak of the pulse current and ignition delay was decreased clearly when testing all additive molecules except the biphenyl. This effect may be explained by the fact that the biphenyl molecules are not polar but can be polarized in an electric field. Because they have two aromatic rings, the molecules will mainly arrange themselves with their axis

parallel to the electrode surface.
When adsorbing an electron, they are keen to distribute this charge between the two aromatic rings, what means in an angle of 90° to the lines of the electric field. In this way, they may obstruct the ignition and breakdown process.

4.2 Electron affinities

n-Alkanes like the n-dodecane have a very low chemical reactivity and also very low electron affinities and very high ionization potentials (Table 6), i.e. they are bad electron acceptors and electron donors, because they need high activation energies.

Aromatic compounds are inclined clearly more strongly to electron transfer reactions. The developing charges are effectively stabilized by delocalisation.

The ionization potentials are degraded also by suitable substituents and the generation is forced by radical cations and radical anions [4]. The shorter ignition delays and lower ignition peaks of the pulse currents are in correlation with the lower ionisation potentials of the aromatic compounds.

Furthermore, the ability of the cyclooctatetraene to carry two charges has a strong negative influence on the pre-ignition and breakdown process. At a pulse current of 5 A as well as 25 A, an ignition was only possible at lowest gap width of 5 µm, even here the ignition delay was very high.

4.3 Effects of molecular size and mobility

It was also supposed that the higher mobility of the smaller additive molecules might have a positive influence on the pre-ignition and breakdown process because polarized benzene molecules would be charge carriers with a high mobility.

By this effect a very fast distribution of the electrical charge was assumed. In contrast to this model the test results have shown a better support of the process by relatively large molecules. This effect could at best be of very little importance.

5 CONCLUSION

The addition of aromatic hydrocarbons to a dielectric fluid consisting of open chained aliphatic hydrocarbons has a distinct influence on the pre-ignition and breakdown phase of single discharges. Especially the larger molecules biphenyl and 2-chloronaphthalene caused very fast ignitions at low ignition peaks of the pulse currents. The main explanation of this effect is their influence on the formation of the outer and diffuse Helmholtz layers. Also the electron affinities of the added molecules have an influence that could especially be observed in the case of the cyclooctatetraene. A positive effect of the higher mobility of smaller polarizable molecules could not be proved.

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