

Project co-financed by the European Union from the European Regional Development Fund

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THE METHOD OF PREPARATION AND USE OF CUTTING FLUIDS BASED ON ORGANIC COMPONENTS

Key words

Cutting fluids, cardanol ethoxylates, glycerol fraction.

Abstract

The specificity of the machining operation, during which the machining fluids have direct contact with the environment and the human body, creates the need to seek solutions that would increase the application of ecologically safe products. An alternative to petroleum and synthetic bases may be vegetable products having good ecological properties. This paper presents a method for producing cutting fluids based on glycerol fraction from the production of biodiesel and a mixture of cardanol ethoxylates and synthetic ester. The produced fluids were studied in terms of their functional properties, which determine their operational suitability as well as their physicochemical and microbiological properties. The wear of a tool bit after working in an environment of such fluids was also determined. It has been found that the cutting fluids, prepared according to the method developed, have preferred functional properties. They meet the performance requirements for these products and can be used in metalworking erosive processes.

Introduction

Because of the detrimental effects of lubricant oils on the environment, there is an increasing interest in products with less ecologically harmful impact [1, 2]. This also applies to technological fluids, primarily those that interact with the environment during machining operations. A very large group of these products are cutting fluids [3–5]. Their annual consumption in Poland is at 8.7 thousand tons of concentrate used as a 5–10% mixture with water. While using cutting fluids, they have direct contact with the human body and the environment. The fluids penetrate the environment through evaporation, during the removal of chips and cut objects and by leaks in installations. The size of losses can reach 30% of the annual consumption of the liquid. Health risks arise due to oil mists formed during the operation and the direct contact with skin [7–9]. Machining fluids, due to the physicochemical composition, are ecologically and dermatologically harmful [10]. Legitimate enterprises, which fit into the worldwide trends of human health and environmental protection, are those that aim to minimize the environmental and health dangers of cutting fluids. There is an increasing interest in replacing the mineral base components with plant and synthetic products [4, 5, 11].

The glycerol fraction, a by-product formed in the process of esterification of the fatty acids of plant oils, in particular rapeseed oil, may be used as a base for cutting fluid [12]. Chemical separation of glycerol fraction is often applied to isolate the crude glycerol, which is characterized by more stable physicochemical properties. Another vegetal product, for which new applications are being searched, is cardanol, cashew shell oil [13, 14]. Due to its strong antiseptic properties, it is advisable to use the product in the production of cutting fluids, due to its basic functional property of a high resistance to microorganisms. Preliminary studies have shown that cardanol has weak lubricating properties. The parameter improved significantly after subjecting the product to oxyethylation [15]. This article presents the physicochemical and microbiological properties of cutting fluids based on chemically purified fraction of glycerol and cardanol ethoxylates.

1. Research object and methods

Two packages of cutting fluids were tested: one having the G1-G3 symbol produced based on chemically purified fraction of glycerol and the other having the C1-C3 symbol based on a mixture of cardanol ethoxylate and synthetic ester. The direct use of ethoxylates as bases of cutting fluids has not been possible due to insufficient stability of ethoxylates and water mixtures. However, the stability was ensured by the use of ethoxylates as a component of binary base containing synthetic ester. The packages G1-G3 and C1-C3 differed in terms of additives.

The cutting fluids were subject to research identifying their physicochemical, microbiological, and technological properties as well as determining the level of their biodegradability. Anti-corrosive properties (PN-M-55789: 1992) and anti-foaming properties (bottle test ASTM D 3519 and blender test ASTM D 3601:1982) for liquids were assessed. Moreover, the value of the pH indicator (PN-EN ISO 10523: 2012), the degree of contamination with bacteria and fungi ("dip slide" method through microbiological samplers) as well as stability (visually) were determined. Resistance to microorganisms was tested on a research stand, which was equipped with a main thermostated tank containing a temperature sensor, electrical stirrer, and a thermometer. The main tank was connected with a contactor tank situated next to the main one, containing steel chips and glass beads. The construction of the stand enabled the circulation of the tested liquid between the tanks. The main tank was able to heat and stir its contents. During the study, 5 percent mixtures of liquid and water were subject to aging processes, and contaminated with the used cutting fluid from the operation, which was characterized by a high content of bacteria $(>10⁷)$. The processes were carried out at a temperature of $36\pm4\degree C$ in 7-hour cycles, repeated every 24 h for 12 weeks. Samples were taken weekly. The changes in the value of pH, anti-corrosive properties, anti-foaming properties and the content of bacteria and fungi were monitored.

The studies on the lubricating properties were conducted in accordance with the requirements of PN-C-04147: 1976. The test elements were spheres with a diameter of $\frac{1}{2}$ inch made of 100Cr6 bearing steel. The size of the defect diameter on the spheres, with a constant load of 392.1 N, speed of 1450 rpm, and time of 1 h was determined.

The biodegradation of the liquid was investigated by the Zahn-Wellens test, in accordance with the guidelines of the OECD 302 B norm.

Technological properties were assessed by the examination of the wear of a tool bit after working in an environment of the fluids under studies. The research was carried out according to the PN-ISO 3685 standard, using tool bits made of P10, P20 and P30 cemented carbide. Shafts having a diameter of $\varphi = 50$ mm and length $l = 500$ mm, made of structural carbon steel of ordinary quality (St 3) alloy steel 40H and stainless steel 0H18N9 were rolled. The study was conducted at a spindle speed of $\omega = 450$ rpm, with a progress of 0.1 mm/rev. and a rolling depth of 1 mm. For each shaft, two passes of the tool bit were used.

2. The method for producing cutting fluids

The process of producing cutting fluids includes the following steps:

• The preparation of input materials for the process of modifying the glycerol fraction and cardanol oxyethylation,

- The separation of glycerol fraction or cardanol oxyethylation,
- Monitoring tests of the produced ethoxylate or the isolated glycerine.
- The preparation of the base and refining additives,
- Base and additive blending,
- The control of physical and chemical properties of the liquid, and
- producing the liquids.

A crucial step in the manufacturing process of cutting fluids is cardanol oxyethylation and the separation of glycerol fraction. The research on the synthesis of ethoxylates allowed identifying the optimal process conditions and catalyst type, which ensures that the product achieved has the most favourable properties. For the preparation of cutting fluids, a product having an average degree of oxyethylation n=6 was selected [15]. The synthesis of ethoxylates was carried out in the presence of NaOH catalyst in an amount of 0.1% calculated on the product, at a temperature of 160°C, at a pressure of 0.25–0.35 MPa. The glycerol fraction was separated by means of formic acid. The acid was used at the concentration of 3% at room temperature. The control parameter of both manufactured products was the refractive index. In order to produce the liquid, output components were prepared using a base and appropriate sets of additives (corrosion inhibitor, biocide, anti-foam lubricant). Next, the blending process was carried out at a temperature $25-30^{\circ}$ C in a container equipped with a low speed mixer. Upon completion, the basic physicochemical properties of the liquid were examined.

3. Overview of the results

Since the cutting fluids are produced as concentrates for dilution with water, the study of physicochemical, microbiological, and lubrication properties was carried out for 5 percent solutions of the tested liquid diluted in water. They were the predicted concentrations of the solutions of operating liquid. For comparison, the commercial water-diluted cutting fluids, which are used in a wide range of processes for deficient metalworking, were examined. They were marked with symbols K1 and K2.

Table 1 presents the research results of physicochemical and microbiological properties of the developed and commercial cutting fluids.

The cutting fluids G1-G3, produced, based on glycerine and C1-C3 based on the mixture of cardanol ethoxylate and synthetic ester, had the physicochemical and microbiological properties similar to the level determined for the commercial products (Tab. 1). They did not show a corrosive effect on steel and cast iron. The pH of the developed and commercial liquids was slightly alkaline (liquids G) and alkaline (liquids C), which was not conducive to the growth of microorganisms. The values of the diameter of the defects on the test spheres, which were determined after the research on the developed

G1-G3 liquids and the commercial K1 and K2, were similar, indicating the same ability to protect against wear caused by friction. In contrast, the anti-wear properties of C1-C3 liquids, which had slightly higher values of the defect diameters, were less effective, but they met the requirements for cutting fluids. All liquids were stable. After 24 hours, there was no delamination of any of them. The developed liquids showed significantly more favourable anti-foam properties than the commercial products, examined by both the bottle and blender tests. None of the cutting fluids contained bacteria and fungi.

Parameter	Cutting fluids							
	G ₁	G ₂	G ₃	C ₁	C ₂	C ₃	K1	K ₂
Anticorrosive properties	H ₀							
pH	7.7	7.7	7.9	9.5	9.0	8.7	9.2	9.0
Anti-wear properties, defect diameter, mm	0.77	0.77	0.60	0.90	1.00	0.90	0.66	0.86
Stability (visually)	s^*							
Anti-foam properties (bottle test), s	2	1	1	1	3	4	20	10
Anti-foam properties (blender test), s	\overline{c}	1	\overline{c}	$\overline{2}$	3	\overline{c}	30	40
number of microorganisms (dip slide):								
bacteria	none							
fungi	none							

Table 1. Physicochemical and microbiological properties of 5 percent solutions of the cutting fluids diluted in water

The developed cutting fluids demonstrated high resistance to microorganisms (Table. 2).

Table 2. Change of physicochemical and microbiological properties of the 5 percent mixtures of the developed cutting fluids diluted in water as a result of their laboratory aging

Parameter		Liquid symbol				
		C1	C2	C ₃		
Total number of bacteria	Before aging	nw^*	nw^*	nw^*		
	After aging	nw^*	nw^*	10 ³		
	Before aging	nw^*	nw^*	nw^*		
Total number of fungi	After aging	nw^*	nw^*	nw^*		
	Before aging	H ₀	H ₀	H ₀		
Anticorrosive properties	After aging	H ₀	H ₀	H ₀		
	Before aging	9.5	8.7	8.9		
pH	After aging	8.7 9.5		8.9		
Anti-foam properties	Before aging	4/40	5/35	5/35		
Bottle test/blender test, s	After aging	5/55	15/60	20/60		

* not identified

As a result of aging, there was no change in the significant physicochemical and microbiological properties of the liquids produced based on glycerine and cardanol ethoxylates (Tab. 2). Bacteria and fungi appeared in none of the cutting fluids. The anticorrosion properties of the liquid did not change. None of them had a corrosive effect on steel and cast iron. In contrast, antifoaming properties slightly deteriorated. The fluids, however, which underwent the aging process, were comparable in this respect to the fresh commercial cutting fluids (Tab. 1). This indicated that the developed liquids met the performance requirements in terms of resistance to microorganisms.

All prepared fluids, both the ones based on the mixture of cardanol ethoxylates and diisooctyl adipate (C) and the ones based on purified glycerol fraction (G) had a high susceptibility to biochemical decomposition (Table 3).

Table 3. The degree of the biodegradation of produced cutting fluids

	Fluid symbol							
	\sim ◡	\sim ◡▵	\sim ັ		G2			
biodegradation degree $[%]$	94.9	92.9	90.0	98.5	99.0	98.8		

Each fluid developed met the criteria of biodegradation process of cutting fluids, according to which the level of biodegradability above 80 percent classifies the fluid to easily biologically degradable products.

The study of technological properties was conducted during the real process of rolling. The test results were expressed using standard geometrical parameters of the tool bit blade wear: KT – the depth of gouge the on the surface, VBB – the average bandwidth of abrasive wear on the contact surface and VBBmax – the highest bandwidth of abrasive wear on the contact surface. They showed similar properties of the developed and commercial cutting fluids (Tab. 4).

Tool bit type/steel	Cutting fluids							
type	G1	G ₂	G ₃	C ₁	C ₂	C ₃	K1	K ₂
	KT [mm]							
P10/ST3	0.64	0.42	N^*	N^*	N^*	0.63	N^*	N^*
P10/4OH	0.33	0.43	N^*	N^*	0.39	0.46	0.35	0.19
P10/OH18N9	0.03	0.11	0.03	N^*	N^*	N^*	N^*	0.01
P20/ST3	0.49	0.13	N^*	0.65	N^*	0.59	0.43	0.37
P20/4OH	0.19	0.30	0.04	N^*	N^*	0.51	0.33	0.26
P30/OH18N9	N^*	0.16	0.04	0.09	$_{\rm N*}$	0.07	N^*	0.04
	Vbb [mm]							
P10/ST3	0.97	0.78	0.70	0.72	0.12	0.80	0.11	0.36
P10/4OH	0.48	0.67	0.44	0.40	0.54	0.65	0.44	0.30
P10/OH18N9	0.01	0.11	0.07	0.05	0.74	0.23	0.03	0.00
P20/ST3	0.91	0.12	0.00	0.88	0.07	0.56	0.82	0.89
P20/4OH	0.30	0.45	0.09	0.51	0.49	0.89	0.56	0.41
P30/OH18N9	0.04	0.14	0.06	0.11	0.03	0.03	0.08	0.08
	Vb_{max} [mm]							
P10/ST3	1.14	0.88	0.97	1.00	0.20	1.05	0.19	0.36
P10/4OH	0.55	0.80	0.99	0.51	0.60	0.83	0.57	0.30
P10/OH18N9	0.01	0.15	0.09	0.09	0.80	0.42	0.05	0.00
P20/ST3	0.98	0.19	0.00	1.17	0.09	1.00	0.97	0.89
P20/4OH	0.39	0.56	0.14	0.57	0.60	1.02	0.66	0.41
P30/OH18N9	0.07	0.16	0.08	0.20	0.04	0.05	0.08	0.08

Table 4. The wear of the tool bit blade while turning various materials in the presence of 5% test solutions of cutting fluids

N* built-up.

The developed cutting fluids, especially the ones based on glycerol, protected the tool bits against wear during machining of OH18N9 stainless steel and 4OH alloy most effectively. The depth of gouge the on the surface and the wear of the contact area of all the tool bits were the smallest. In this respect, the effectiveness of the G1-G3 liquids was similar to the commercial K2 liquid. Tool bit wear during the machining of the same kind of steel with the use of commercial liquid K1 was greater. However, the use of the liquids developed to process standard quality steel resulted in higher values of the tool bit wear indicators in relation to K2 liquid and similar values to those obtained for K1 liquid.

Conclusions

The results showed that cardanol ethoxylates and glycerine might constitute the basic components of cutting fluids. The liquids based on them could be characterized by high physicochemical, microbiological, and technological

properties. They were similar and sometimes surpassed commercial products in this respect. Both the purified glycerol-based liquids and the mixtures of cardanol ethoxylate and synthetic ester showed a high stability of chemical composition and resistance to bacteria and fungi. They were characterized by high anticorrosive and anti-foam properties. The liquids sufficiently protected cutting tools against wear, especially in processing high quality steel. The use of plant products as a base and additives having low ecotoxicity and relatively high biodegradability provided a high degree of biodegradation of the liquids produced. This is very important for the environment due to the nature of the operation of cutting fluids. Therefore, it can be concluded that these waste products (glycerol fraction and cardanol) can provide the raw materials for the core components of cutting fluids. The cutting fluids based on these components can be applied in the metalworking erosive processes.

Scientific work executed within the Strategic Programme "Innovative Systems of Technical Support for Sustainable Development of Economy" within Innovative Economy Operational Programme.

References

- 1. Orloff K., Falk H.: An international perspective on hazardous waste practices. Interantional Journal of Hygiene and environmental Health. 2003, 206, pp. 291–302.
- 2. Chaaban A. Moustafa.: Hazardous waste source reduction in materials and processing technologies. Materials Processing Technology, 2001, 119, pp. 336–343.
- 3. Pettersson A.: High-performance base fluids for environmentally adapted lubricants. Tribology International, 2007, 40, pp. 638–645.
- 4. Jayadas N.H., Prabhakaran Nair K., Ajithkumar G.: Tribological evaluation of coconut oil as an environment-friendly lubricant. Tribology International, 2004, 40, pp. 350–354.
- 5. Erhan S.Z., Asadauskas S.: Lubricant basestocks from vegetable oils. Industrial Crops and Prodicts, 2000, 11, pp. 277–282.
- 6. Podniadło A.: Paliwa, oleje i smary w ekologicznej eksploatacji. WNT, Warszawa 2002.
- 7. Cheng Ch., Phipps D., Alkhaddar R.M.: Reviev. Treatment of spent metalworking fluids. Water Research, 2005, nr 39, pp. 4051–4063.
- 8. Cyprowski M. i inni.: Szkodliwe działanie czynników biologicznych uwalnianych podczas procesów obróbki metali z użyciem chłodziw. Medycyna Pracy, 2006, 57 (2), s. 139–147.
- 9. Cyprowski M.: Zanieczyszczenia mikrobiologiczne cieczy obróbkowych. Bezpieczeństwo Pracy, 2012, nr 9, s.16–19.
- 10. Musialek K. i inni.: Badania niektórych właściwości środowiskowych i technologicznych świeżych i zużytych emulsji stosowanych w obróbce skrawaniem. Paliwa, oleje i smary w eksploatacji, 2003, nr 108, s. 21–29.
- 11. Bartz W.J.: Ecotribology: environmentally acceptable tribological practices. Tribology International. 2006, 39, pp. 728–733.
- 12. Gaca J.: Frakcja glicerynowa po produkcji biodiesla odpad czy surowiec. Czysta Energia, 2006, 11.
- 13. Vasapollo G. i inni: Cardanol-Based Materials as Natural Precursors for Olefin Metathesis. Molecules, 2011, nr 16, pp. 6871–6882.
- 14. Rodrigues F. i inni.: Antioxidant Activity of Cashew Nut Shell Liquid (CNSL) Derivatives on the thermal Oxidation of Synthetic cis-1-4- Polysoprene. J.Broz.Chem.Soc. 2006, nr 2, pp. 265–271.
- 15. Naraniecki B., Lukosek M., Rogoś E., Kosno J.: Badania oksyetylacji kardanolu oraz właściwości oksyetylatów. Przemysł Chemiczny, 2012, nr 10, s. 1000–1005.

Metoda wytwarzania i zastosowanie cieczy obróbkowych na bazie składników ekologicznych

Słowa kluczowe

Ciecze obróbkowe, oksyetylaty kardanolu, frakcja glicerynowa.

Streszczenie

Specyfika eksploatacji, podczas której ciecze obróbkowe mają bezpośredni kontakt z otoczeniem i organizmem człowieka, generuje potrzebę poszukiwania rozwiązań zwiększających aplikację produktów bezpiecznych ekologicznie. Alternatywą dla baz naftowych i syntetycznych mogą być produkty roślinne charakteryzujące się dobrymi właściwościami ekologicznymi. W artykule przedstawiono metodę wytwarzania cieczy obróbkowych na bazie frakcji glicerynowej z produkcji biodiesla oraz mieszaniny oksyetylatu cardanolu z syntetycznym estrem. Zbadano właściwości funkcjonalne wytworzonych cieczy, decydujące o ich przydatności eksploatacyjnej, a także ich właściwości fizykochemiczne i mikrobiologiczne. Określono także zużycie noża tokarskiego po obróbce w środowisku tych cieczy. Stwierdzono, że ciecze obróbkowe, wytworzone według opracowanej metody, charakteryzują się korzystnymi właściwościami funkcjonalnymi. Spełniają wymagania eksploatacyjne dotyczące tego rodzaju produktów i mogą być stosowane w procesach ubytkowej obróbki metali.