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THE ASSESSMENT OF THE FUNCTIONALITY OF BIO-ANTIOXIDANTS IN INDUSTRIAL EXPLOITATION FLUIDS

Key words

Thermo-oxidation, natural antioxidants, oil stability.

Abstract

The paper presents the results of a preliminary study designed to assess the possibilities of the use of natural antioxidants in industrial exploitation fluids. As a result of the analysis of biochemical mechanisms and literature research within the scope of the application of natural antioxidants in food products and cosmetics, silymarin was selected for laboratory testing as a preparation being characterized as potentially the most efficient antioxidant among the other substances taken into consideration, i.e. tocopherols, ubiquinone, and silymarin. Laboratory tests were performed with the aid of a Petrooxy apparatus, using accelerated oxidation method at 140°C. Compositions containing 0.5, 1.0, 1.5, and 2.0% (m/m) of silymarin in mineral oil were tested. It was found that the introduction of 1% (m/m) bio-additive causes the best antioxidant effect among the studied compositions.

Introduction

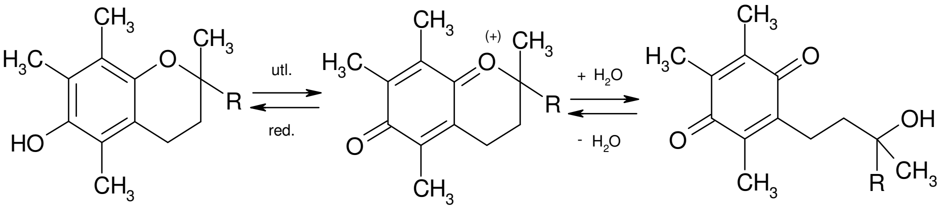
Today, the increasingly strict requirements of the European Union within the scope of environmental protection, and the necessity to use the best available techniques (BAT), stimulate the activity of the Member States and pose the incentive to search for new environmentally friendly technological solutions. These actions also relate to the area of work on the ecological exploitation fluids, which include industrial oils, in particular hydraulic and machine oils. These types of oils are exposed to both mechanical forces, chemical and thermal influences in the course of routine operation. It is worth mentioning that chemical changes in the oils occur mainly due to destructive processes, including thermo-oxidation [1, 2].

Therefore, a key issue that determines the service life of industrial oils is the improvement of their thermal and oxidative resistance. Shaping the oxidative stability is possible, inter alia, through the introduction of appropriate upgrading additives to the oil base. Their efficiency depends mainly on their chemical structure, their quantity share, and the nature of their impact on the oil base. Typical antioxidant additives are synthetic materials, among which are phenols, zinc dialkyldithiophosphates, aromatic amines, sulphides, organic sulphides, dialkyldiaminomethane, zinc, antimony, and bismuth dialkyldithiocarbamates [3–7].

Nevertheless, it is necessary to search for other substances, in particular of natural origins, which would increase the ecological nature of oil products by boosting the biodegradability and by eliminating harmful metallic elements from the molecular structures of the used additives, and they would simultaneously have efficient antioxidant effect.

1. Mechanisms of action of selected natural antioxidants

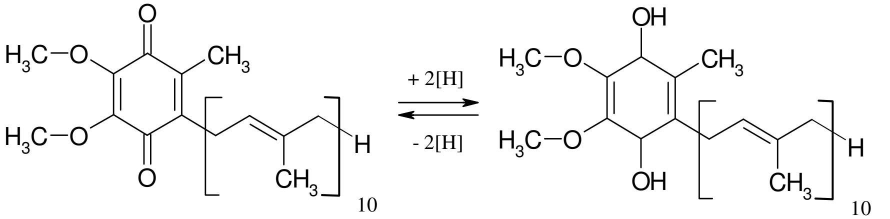
Natural chemical compounds, which show antioxidant action and are soluble in non-aqueous media, include silymarin, tocopherols, and the derivatives of cardol, and coenzyme Q10 (ubiquinone) [4, 8, 9]. The mechanism of action of these compounds is well researched for the biochemical processes that take place in the cells of living organisms. For example, the antioxidant effect of tocopherols is described as a transfer of phenolic hydrogen into free peroxyl radical of peroxidized and polyunsaturated fatty acid. The initial product of tocopherol oxidation is a chemically unstable tocopheroxyl radical group that may be either reduced to tocopherol through co-antioxidants or may react with another radical and form tocopherolquinone, as shown in the following reaction:



tokoferol tokoferolo-p-chinon

Tocopherols are resistant to elevated temperatures (up to 200°C). It was also found that tocopherols in living organisms are subject to regeneration with participation of co-antioxidants, such as ascorbate and glutathione. It was further found that ubiquinone 10 (coenzyme Q10) protects α-tocopherol against photooxidation. Therefore, the lack of such co-antioxidants in living organisms can limit the properties of tocopherols.

Ubiquinone is almost in all living cells, except the cells of some bacteria and fungi. Its concentration in living organisms is very varied. Ubiquinone is located mainly in the inner membrane of the mitochondrion. It was believed that ubiquinone was only involved in the processing of energy, but the discovery of ubiquinone in intracellular membranes showed its antioxidant properties, associated with reversible redox reactions, which may be described by the following scheme [4]:

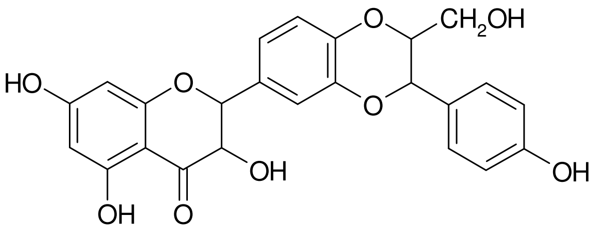


ubichinon ubihydrochinon

Coenzyme Q10 prevents the formation of free radicals and shows good properties of "a free radicals scavenger." It is a strong antioxidant and is an essential substance in the process of energy production. Acting as an antioxidant ubiquinone reduces the "oxidative stress" and prevents cells of living organisms from aging processes by inhibiting their division.

It also reduces oxidative damage caused by UVA radiation, preventing the breakdown of collagen. This formulation has found industrial application as an antioxidant in many cosmetic and food products. However, it is unstable at high temperatures, which cause its destruction. Hence, its application in the industrial oils operating in high temperatures may be limited [10].

Another natural antioxidant, relatively easily extracted from the plant material, is sily-marin, which is a mixture of flavonoid compounds [11]. It consists of silybin (silibinin), sily-dianin (silydionin), and silykristin (silychristin). The first known and structurally well-defined component of silymarin was silybin, which is about 50% silymarin and is the main antioxidant constituent having the following structural formula:



Due to its molecular structure, silymarin is able to capture free radicals, which means it has powerful antioxidant properties. Together with radicals, silymarin forms stable intermediate products of lower reactivity. Due to its antioxidant properties, it breaks chain reactions in living organisms, thereby preventing the damage of cell membranes. It is one of the most effective natural antioxidants and protectors that enhance immunity. Up to now, the results of experiments have confirmed the effectiveness of silymarin as an antioxidant used for the enrichment and stabilization of industrial products, in particular, food and cosmetic products [11]. The positive effects of the industrial applications of this type of natural antioxidants in food products, for example, encourage to attempt to start using them in the technology of composing modern, environmentally friendly, industrial exploitation fluids.

The aim of the study was to assess the effectiveness of silymarin preparation obtained from the endosperm of milk thistle (Silybum marianum), which is a waste product from the production technology of pharmaceuticals, which was used as an antioxidant in the mineral base oils.

2. The research methodology

Silymarin, constituting a natural antioxidant, was used in the study. Importantly, the used oil originated from the endosperm, which is a by-product obtained during the processing of milk thistle seeds, used in the manufacture of pharmaceutical products and cosmetics. This product was prepared at the Institute of Industrial Chemistry in Warsaw. The preparation was introduced to SN 400 mineral oil, produced in the process of refining crude oil.

Oil compositions were then prepared containing 0.5%, 1.0 %, 1.5%, and 2.0% [m/m] of silymarin, respectively. The concentration range of the antioxidant additive was selected at a level close to the concentration of typical additives contained in the oil compositions used in practice in industry.

Oxidation resistance tests were conducted with the use of PetroOXY apparatus, produced by the Petrotest Company, under the following test conditions: sample volume of 5.5 ml, the process temperature of 140°C, and the initial filling pressure of 700 kPa. As an oxidizing agent, oxygen with a purity of 99.9% was used. It was dosed into the measuring chamber at a pressure of 8 bars. The time necessary to obtain a maximum pressure drop in the value of the test sample by 10% was determined. The final result constituted the arithmetic mean of the two measurements results.

3. The analysis and research results

Figure 1 and 2 show an exemplary dependency between the pressure in the measuring chamber and the test time for the model samples, composed of SN 400 mineral-based oil.

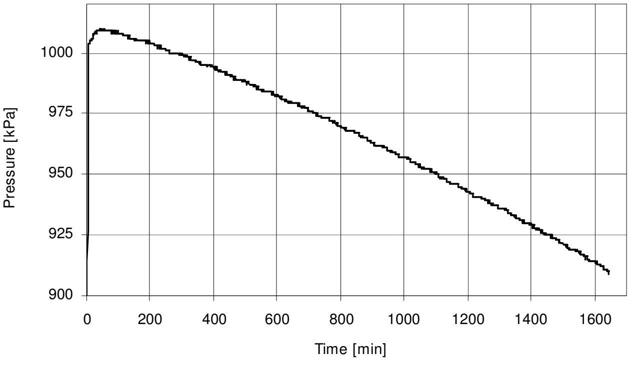


Fig. 1. The dependency line chart of the pressure in the measuring chamber towards the thermo-oxidation time of the SN 400 oil containing 1% (m/m) of silymarin

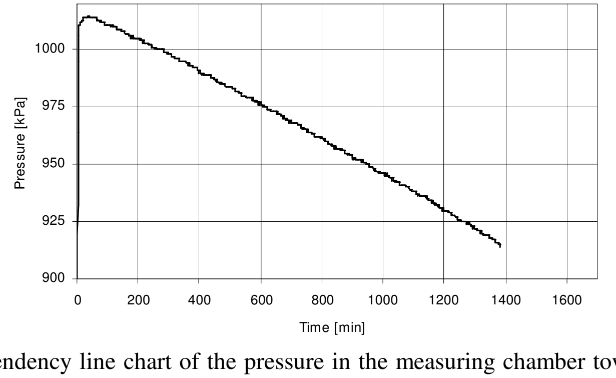


Fig. 2. The dependency line chart of the pressure in the measuring chamber towards the thermo-oxidation time of the SN 400 oil containing no silymarin

The comparison of registered curved lines clearly demonstrates that the composition containing silymarin has a higher oxidative stability, which is connected with longer oxidation induction time by more than 200 minutes, which was recorded for oil enriched with the addition of an anti-oxidizing agent.

The combination of the research results showing the dependency of the oxidation induction time towards silymarin content in mineral oil is shown in Figure 3.

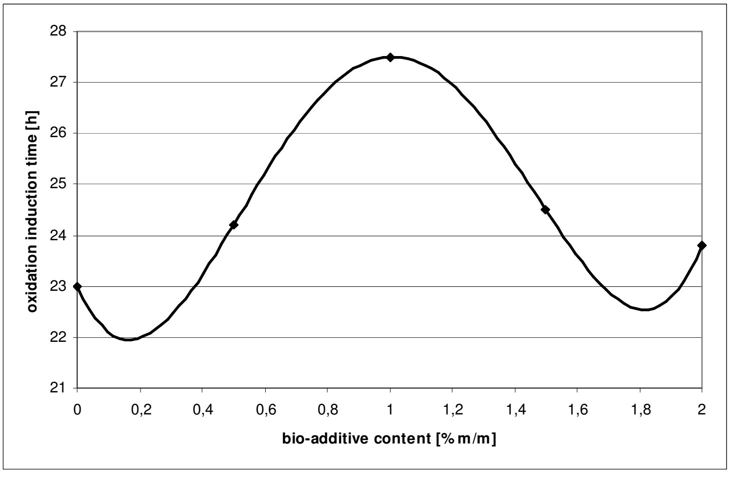


Fig. 3. The dependency line of the oxidation induction time of the model compositions based on SN 400 mineral oil towards its silymarin content

Based on the obtained results, it can be concluded that, in the case of a composition containing silymarin, its thermo-oxidative resistance increases in comparison to the starting oil base, because of the introduction of a small amount of natural antioxidant (i.e., 0.5% m/m). However, the introduction of 1% of silymarin to the oil base increases the thermo-oxidative stability of the composition by 19% in comparison to the starting base. A further increase in the silymarin content in mineral oil does not enhance the oxidative stability of the oil. The analysis and the results of preliminary laboratory tests indicate a high potential of natural antioxidants concerning their use in the technology of composing biodegradable industrial oils. However, it is necessary to examine the accompanying chemical reactions as well as their kinetics. This will allow the researcher the rational design of the composition contents containing natural antioxidants.

Summary

The analysis of biochemical mechanisms and the preliminary studies of selected bio-antioxidants (tocopherols, ubiquinone) indicate a limited application in industrial exploitation fluids used at high temperatures. Among the tested bio-antioxidants, silymarin gives promising results. As a result of experimental research in the accelerated oxidation conditions, it was found that the introduction of silymarin in an amount of 1% causes an improvement in the oxidative stability of the mineral oil by about 19% in comparison to the non-improved oil base.

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

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Ocena funkcjonalności bio-antyoksydantów w przemysłowych płynach eksploatacyjnych

Słowa kluczowe

Termooksydacja, naturalne antyoksydanty, stabilność olejów.

Streszczenie

W artykule przedstawiono wyniki wstępnych badań, których celem była ocena możliwości wykorzystania naturalnych antyoksydantów w przemysłowych płynach eksploatacyjnych. W wyniku analizy mechanizmów biochemicznych oraz doniesień literaturowych w zakresie aplikacji naturalnych antyoksydantów w produktach spożywczych i kosmetycznych wybrano do testów laboratoryjnych sylimarynę jako preparat o potencjalnie największej efektywności antyoksydacyjnej spośród rozważanych substancji, tj.: tokoferoli, ubichinonu oraz sylimaryny. Testy laboratoryjne zrealizowano przy pomocy aparatu Petrooxy, stosując metodę przyspieszonego utleniania w temperaturze 140°C. Badano kompozycje zawierające 0,5; 1,0; 1,5 oraz 2,0% (m/m) sylimaryny w oleju mineralnym. Stwierdzono, iż wprowadzenie 1% m/m biododatku powoduje najlepszy efekt przeciwutleniający wśród zbadanych kompozycji.