Mandziuk I.,
Prisyazhna K.
Khmelnytskyi National University,
Khmelnytskyi, Ukraine
E-mail: imandzyk@ukr.net

THE BASES FOR LUBRICATING MATERIALS SYNTHESISED BY TECHNOLOGIES OF THERMOPLASTIC WASTE RECYCLING

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It was offered an effective method of estimating oxidation susceptibility of fats and lubricants with the use of the results of rheometric investigations of changes in effective viscosity with a rotational viscometer. A mixture of amine and phenolic high-molecular compounds should be considered as the most effective antioxidant for natural fats with a glance of features of chemical processes accompanying their oxidation.

Keywords: oxidation susceptibility, natural vegetable and animal fats, antioxidants.

Introduction

Rise of new technologies, structures, machines and mechanisms is one of the components of technological advance. Their working capacity is ensured by application of lubricating materials. At present lubricating materials are considered as important elements of any mechanism.

European strategic development in the XXI century suggests implementation of the following principles of "green tribology": energy conservation and material saving, environmental improvement. Most of lubricants used today are manufactured on the basis of oil and the products of its processing (mineral and synthetic oils). Taking into consideration the requirements advanced by "green tribology", we can state that one of the tasks is extending the use of natural biodegradable lubricants. Natural vegetable and animal fats fully satisfying the requirements of environmental safety can make the base of such materials. The main defect of this group of materials pointed out by many researchers is a low oxidation resistance in use.

A team of researches guided by I. Padgurskas studies in detail the possibility of using animal fats as a base for lubricating materials [3]. Modification of vegetable oils by metal nanoparticles [4, 5] and changes in tribological characteristics of oils in the process of oxidation [3] have been investigated. The influence of natural vegetable compounds – Sage attar, Thyme attar has been studied as an oxidation stabilizer.

The majority of publications relating to studies of fat oxidation resistance use the acid value as a quantitative factor, and it is rarely complemented with the peroxide number. Free fatty low-molecular acids are discoursed in commentaries to the interpretation of oxidation processes in lubricants. With the aptitude of a free radical chain mechanism of fat oxidation with degenerate chain branching [1, 2] free acids arise in deep stages of oxidation as independent products. It demands considerable accumulation in the system of hydroperoxides. Two main categories of processes of oxidation of hydrocarbons and lipids are singled out:

- rmation of condensed ligation products with involvement of alkyl radicals;
- composition of starting material to low-molecular spirits, ketones, and acids with involvement of peroxide radicals [6].

It is quite clear that considerable accumulation of acid groups in an oxidized material is preceded by serious changes in structural characteristics of a material; in particular a change in the viscosity of the system occurs in lubricating materials. In case of ligation processes caused by the oxidation the viscosity increases, and in case of oxidation decomposition the viscosity decreases.

Thus, using the parameter of "acid value" we point to the accomplished fact of irreversible processes occurring in a material in the process of oxidation.

In the process of using antioxidants neutralizing both alkyl and peroxide radicals the acid value becomes even more diverse.

We make an assumption that effective dynamic viscosity can be more informative and correct for the description of oxidation processes occurring in lubricating materials. Kinematic viscosity of a base used by many companies for lubricants specifications is not sufficiently informative. Kinematic viscosity is not defined for grease lubricants containing an additive packet.

Purpose and setting objectives

The research is aimed at carrying out rheometric investigation of natural vegetable and animal fats with the view of estimating efficiency of synthetic antioxidants.

Experimental part

The following research methods were used in the work:

- rheometric investigation – dependence of dynamic viscosity on the temperature and the rate of change in shear deformation was studied with the use of Brookfield Viscometer CAP 2000$^+$;
- acid number ISO 660:2000 (State Standard 4350:2000).

The objects under study:
- beef fat – State Standard 25292-82;
- chicken fat – State Standard 54676-2011;
- rapeseed oil – State Standard 53457-2009;
- sunflower oil – State Standard 4492:2005;
- antioxidants of various classes and groups produced by BASF Company: Irganox L115, Irganox L64, Irganox L06, Irganox L150, Irganox L109.

The amount of antioxidant was 0.3% wt. Oxidation resistance of fats was evaluated according to State Standard 5734-76 suggesting that oxidation resistance be defined as a difference in the acid value of initial fat and fat after oxidation. Since the reference value of the mass fraction of free acids of the fats under study is different, we suggest calculating the relative value of change of the mass fraction of free acids (A.V.) of fat before and after the tests in order to eliminate the influence of this factor (oxidation susceptibility):

$$Apt = \frac{A.V._{of\ fat\ after\ testing} - A.V._{initial\ fat}}{A.V._{initial\ fat}}. \quad (1)$$

The less the value of Apt (oxidation susceptibility) of fat or fat-based lubricants is, the less the degree of material oxidation is.

Rheometric investigation involved the following measurements:
- of dynamic viscosity $\eta = f(T)$ within the temperature range of +50÷140 °C at the cone rotational frequency of 100 rpm;
- of dynamic viscosity $\eta = f(\dot{\gamma})$ at the rate of shear deformation changing from 1333 to 10677 s^{-1}.

The results of rheometric investigation of initial beef fat and beef fat after oxidation are presented in figures 1 - 2.

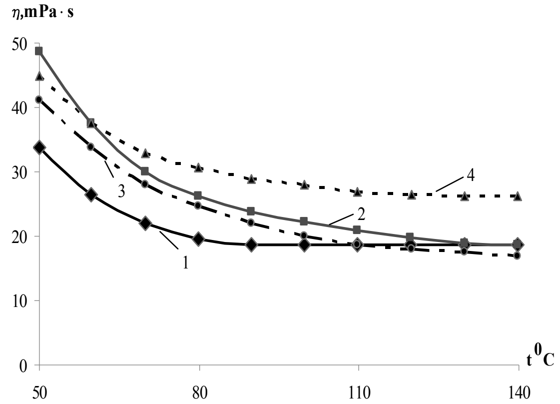

Fig. 1 – Dependence of viscosity on temperature (at $\dot{\gamma}$ = 1300 s^{-1}) for animal fat:
1 – initial beef fat; 2 – beef fat after oxidation; 3 – beef fat after oxidation with Irganox L64; 4 – beef fat after oxidation with Irganox L115

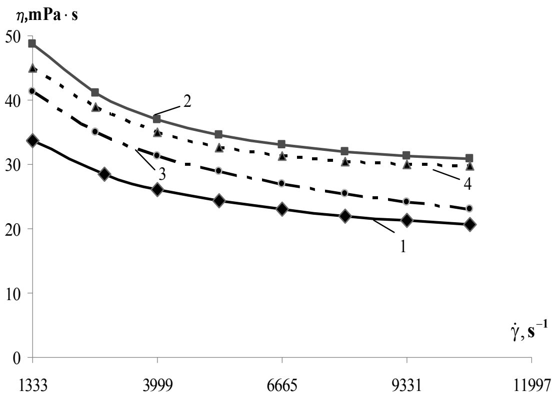

Fig. 2 – Dependence of viscosity on the shear rate (at 50 °C) for animal fat:
1 – initial beef fat; 2 – beef fat after oxidation; 3 – beef fat after oxidation with Irganox L64; 4 – beef fat after oxidation with Irganox L115

To estimate the effect of oxidation processes on the change in dynamic viscosity on the analogy of formula (1) we calculated the value of oxidation susceptibility in terms of the results of measuring viscosity depending on temperature (2) and viscosity depending on the rate of shear deformation (3):

$$Apt_{\eta_T} = \frac{{}^{\eta}T_0 - {}^{\eta}T_i}{{}^{\eta}T_i}, \quad (2)$$

$$Apt_{\eta_{\dot{\gamma}}} = \frac{\eta_{\dot{\gamma}_0} - \eta_{\dot{\gamma}_i}}{\eta_{\dot{\gamma}_i}}, \quad (3)$$

where Apt_{η} – oxidation susceptibility calculated in terms of change in viscosity depending on temperature;

Apt_{η_T} – oxidation susceptibility calculated in terms of change in viscosity depending on shear deformation;

${}^{\eta}T_0$ – the values of change in viscosity depending on the temperature of oxidized material at a selected temperature;

${}^{\eta}T_i$ – the values of change in viscosity depending on the temperature of a virgin sample at the same temperature;

${}^{\eta}\dot{\gamma}_0$ – the values of change in viscosity of oxidized material depending on the rate of shear deformation at a selected value of shear deformation;

${}^{\eta}\dot{\gamma}_i$ – the values of change in viscosity of starting material depending on the rate of shear deformation at the same value of shear deformation.

The calculation was performed for viscosity values at 50 °C и 100 °C using formula (2).

To perform the calculations using formula (3) we selected reference values of shear deformation of 1330 s^{-1} (100 rpm) and 10667 s^{-1} (800 rpm).

Charts describing oxidation susceptibility of initial natural fats and fats containing antioxidants on the basis of the results of change in the acid value (formula 1) are presented in figures 3, 4.

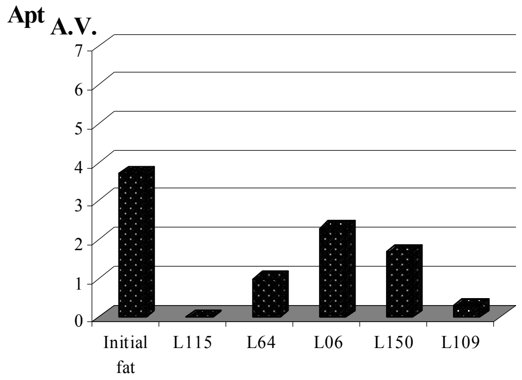

Fig. 3 – Oxidation susceptibility of beef fat calculated in terms of the acid value depending on the nature of an antioxidant

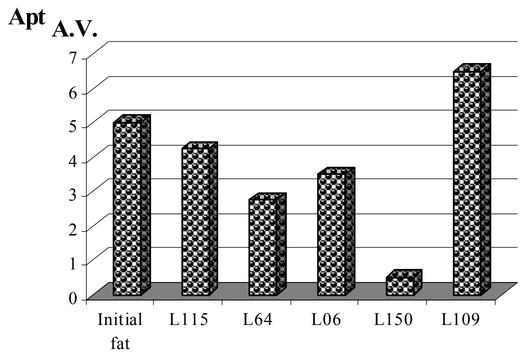

Fig. 4 – Oxidation susceptibility of chicken fat calculated in terms of the acid value depending on the nature of an antioxidant

The analysis of obtained results evidences our conclusion [7] that beef fat shows the least oxidation susceptibility (fig. 5, 6), sunflower oil is less resistant (fig. 7, 8).

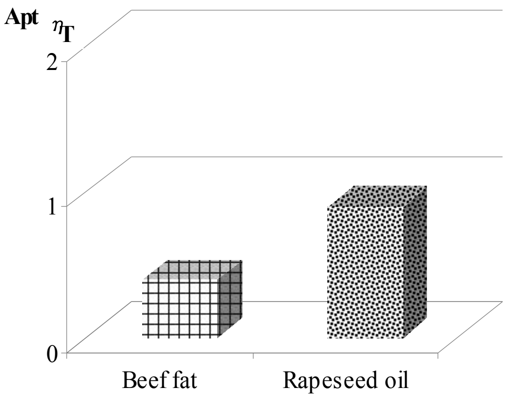

Fig. 5 – Oxidation susceptibility of fats calculated in terms of change in viscosity depending on temperature ($\dot{\gamma}$ = 1333 s^{-1}), calculation point is 50 °C

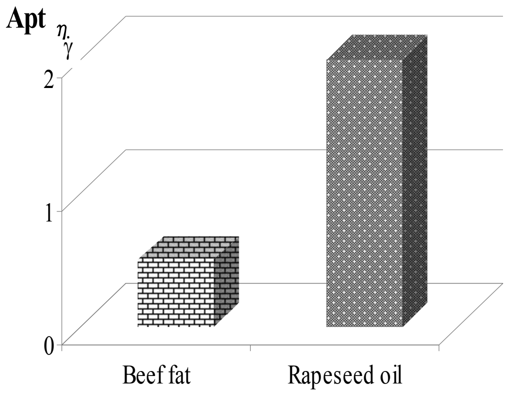

Fig. 6 – Oxidation susceptibility of fats calculated in terms of change in viscosity depending on shear rate (t = 50 °C), calculation point is 10667 s^{-1}

The investigations show that the following antioxidants are the most effective oxidation inhibitors for beef fat: Irganox L115 – a high-molecular phenolic antioxidant containing thioester groups, and Irganox L109 – a high-molecular antioxidant. The most effective oxidation inhibitor for chicken fat is Irganox L150 – a mixture of amine and phenolic high-molecular compounds. Irganox L150 and Irganox L64, which are also a mixture of amine and phenolic high-molecular compounds, are the most effective for vegetable oils (fig. 7, 8).

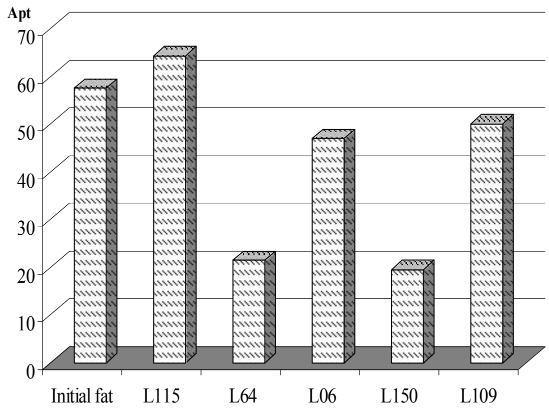

Fig. 7 – Oxidation susceptibility of sunflower oil calculated in terms of the acid value

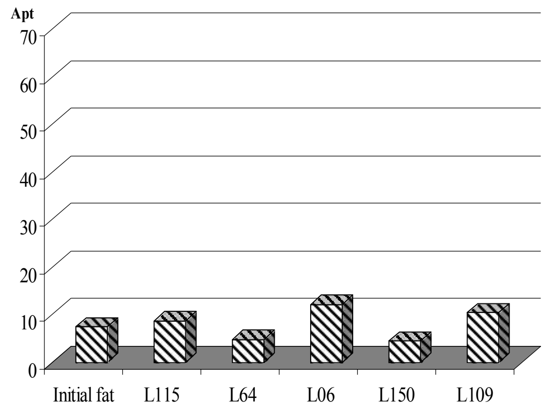

Fig. 8 – Oxidation susceptibility of rapeseed oil calculated in terms of the acid value

The calculation of oxidation susceptibility based on the results of rheometric measurements for various types of antioxidants makes it possible to ascertain that the most effective oxidation inhibitors for natural fats are Irganox L150 and Irganox L64 – mixtures of amine and phenolic high-molecular compounds (fig. 9, 10).

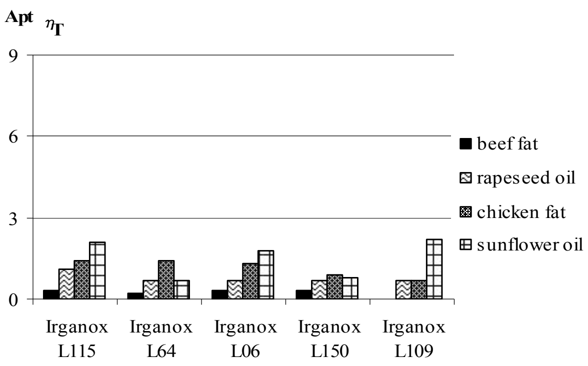

Fig. 9 – Oxidation susceptibility of fats with various antioxidants calculated in terms of change in viscosity depending on temperature ($\dot{\gamma}$ = 1333 s^{-1}), calculation point is 50 °C

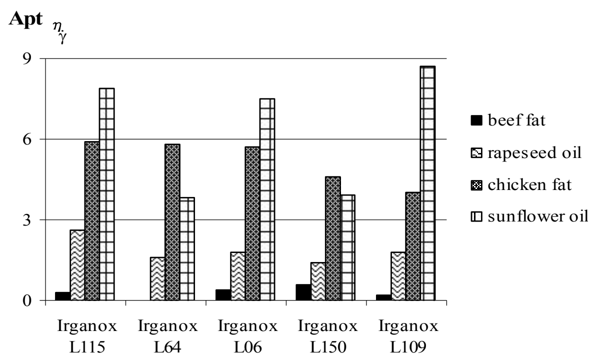

Fig. 10 – Oxidation susceptibility of fats with various antioxidants calculated in terms of change in viscosity depending on shear rate (*t* = 50 °C), calculation point is 10667 s^{-1}

It should be noted that oxidation susceptibility calculated in terms of the acid value for sunflower oil is higher than oxidation susceptibility calculated for rapeseed oil (fig. 7, 8). At the same time, samples of sunflower oil, both initial and containing antioxidants, became gellike after tests on oxidation resistance. Thus, acid value does not always make it possible to obtain reliable information about changes in fats and lubricants after their oxidation.

Conclusions

The studies done by us enable us to suggest an effective method of estimating oxidation susceptibility of fats and lubricants with the use of the results of rheometric investigations of changes in effective viscosity with a rotational viscometer.

A mixture of amine and phenolic high-molecular compounds should be considered as the most effective antioxidant for natural fats with a glance of features of chemical processes accompanying their oxidation.

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Мандзюк И., Присяжная К. **Базовые основы смазочных материалов, синтезированных по технологиям рециклинга отходов термопластов.**

Предложен эффективный метод оценки восприимчивость жиров и смазочных материалов к окислению на основании результатов исследований реометрических измерений изменения эффективной вязкости с помощью ротационного вискозиметра.

Изучено влияние различных классов антиоксидантов на величину восприимчивости к окислению природных жиров. Установлено, что наиболее наиболее эффективным антиоксидантом для натуральных жиров является смесь аминсодержащих соединений и фенольных высокомолекулярных соединений..

Ключевые слова: восприимчивость к окислению, натуральные растительные и животные жиры, базовые основы консистентных смазок, антиоксиданты.