

Article citation info:

Bukrejewski P, Wardzińska P. The influence of copper on the oxidation stability of commercial diesel oil. The Archives of Automotive Engineering – Archiwum Motoryzacji. 2016; 72(2): 5-14, <http://dx.doi.org/10.14669/AM.VOL72.ART7>

THE INFLUENCE OF COPPER ON THE OXIDATION STABILITY OF COMMERCIAL DIESEL OIL

PAWEŁ BUKREJEWSKI¹, DOROTA WARDZIŃSKA²

Automotive Industry Institute (PIMOT)

Summary

Diesel oil as a fuel for compression ignition engines should meet the requirements laid down in the Regulation of the Minister of Economy of 9 October 2015 on the quality requirements for liquid fuels (Dz. U. of 2015, item 1680). Reports of UOKiK (the Office for Competition and Consumer Protection) reveal that a significant part of the diesel oil samples taken at filling stations do not meet the requirements for fuel resistance to oxidation. It is fuel manufacturers' responsibility to ensure that the products sold by them are in conformity with the requirements laid down in the applicable normative documents; hence, factors adversely affecting fuel properties most likely occur in the fuel distribution chain. This may be caused by interactions between the fuel and the materials used for the construction of fuel storage tanks and handling equipment. Within the work described herein, the influence of copper on the oxidation stability of commercial diesel oil was examined.

Keywords: diesel oil, copper, oxidation stability

1. Introduction

The oxidation stability, i.e. fuel resistance to degradation processes and to deterioration in quality properties, is one of the basic operational characteristics determined for fuels for compression ignition (CI) engines [13]. In the case of commercial diesel oils, their stability during storage is affected by, inter alia, the proportion of biocomponent, i.e. fatty acid methyl esters (FAME), in the oil. The chemical nature of such esters differs from that of hydrocarbons, which are the basic component of the diesel oils manufactured at present [6]. The 7% (V/V) proportion of FAME in diesel oil with very low sulphur content reduces the

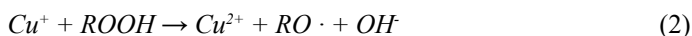
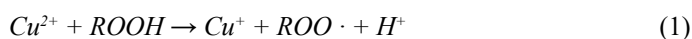
¹ Automotive Industry Institute, Analytical Laboratory, ul. Jagiellońska 55, 03 301 Warszawa, Poland; e mail: p.bukrejewski@pimot.eu

² Automotive Industry Institute, Analytical Laboratory, ul. Jagiellońska 55, 03 301 Warszawa, Poland; e mail: d.wardzinska@pimot.eu

oxidation stability of the fuel during storage, distribution, and use [14]. The oxidation of diesel oils with FAME content is a complex process, which probably runs in accordance with the radical mechanism. The oxidation process begins from the formation of peroxides and hydroperoxides, participating in the mechanism of formation of secondary oxidation products such as aldehydes, organic acids of low molecular mass, and high molecular mass oligomers of fatty acids, which block fuel filters [2]. The thermal, oxidation, and thermo-oxidation stability of diesel oil and its chemical reactivity depend on the chemical and fractional composition of the diesel oil and on the quality and proportion of FAME as a biocomponent in the blend [14].

The fuel oxidation processes may be affected by metal ions, including copper ions, which form organic copper compounds [7].

The literature concerning this subject includes publications that show the influence of the presence of copper ions on the rate of the process of fuel oxidation at raised temperatures [3, 5, 11]. In publication [15], the Walling's research team has proposed a theory that the copper cations present in the fuel directly react with hydroperoxides generated in result of the oxidation of fuel components and form very reactive radicals $ROO\cdot$, $R\cdot$, which are responsible for further fuel degradation:



On the other hand, the copper ions present in the fuel may act as an inhibitor and hamper the oxidation processes by converting the reactive radicals into ions that are not involved in the oxidation reactions. The action of copper as an accelerator or inhibitor depends on the copper concentration in the fuel. It is usually assumed that the copper ions act as inhibitors when their concentration is less than 250 ppm [4].

Copper is a component of the materials used for the construction of pipelines in process installations at filling stations. As an example, the suction, pressure, drain, or vent pipelines are often made of copper pipes. Therefore, the diesel oil present at filling stations is exposed to contact with this material. In consideration of the fuel quality problems signalled by UOKiK (the Office for Competition and Consumer Protection), a research work was done to determine the impact of copper on the oxidation stability of commercial diesel oil with FAME content at temperatures corresponding to the real conditions prevailing at filling stations.

2. Materials and methods

2.1. Materials

The tests were carried out with the use of copper sheet plates with a chemical composition as presented in Table 1.

Table 1. Chemical composition of the copper sheet used for the tests

Material grade	Standard specifications	Chemical composition (% by mass)			
		Cu	Bi	Pb	O
Copper sheet CuETP	EN 13559	99.90 min.	0.0005 max.	0.0005 max.	0.04 max.

The plates were polished with abrasive paper with various grain sizes. Afterwards, their surfaces were degreased by washing with acetone.

As the material used for the tests, commercial diesel oil was used, which was purchased at a filling station chosen at random. The physicochemical properties of the oil have been specified in Table 2.

Table 2. Selected physicochemical properties of the diesel oil used for the tests

Parameter	Test method	Unit	Test result
Density at 15 °C	PN-EN ISO 12185:2002	kg/m ³	834.8
Cold filter plugging point (CFPP)	PN-EN 116	°C	-18
Fractional composition			
(course of distillation):		PN-EN ISO 3405:2012	
Initial boiling point		°C	174.4
10 % (V/V) point		°C	206.7
50 % (V/V) point		°C	275.7
90 % (V/V) point		°C	341
95 % (V/V) point		°C	356.9
% distilled at 180 °C		% (V/V)	0.7
% distilled at 250 °C		% (V/V)	35.3
% distilled at 340 °C		% (V/V)	89.6
% distilled at 350 °C		% (V/V)	93.4
% distilled at 360 °C		% (V/V)	95.7
% distilled, total		% (V/V)	96.7
Final boiling point		°C	361.9

2.2. Testing system

To examine the influence of copper on the oxidation stability of diesel oil, test sample sets were prepared, consisting of 16 borosilicate glass flasks of 1 dm³ capacity each. Every flask was filled with a measured quantity of 1 dm³ of diesel oil, to minimize the amount of air left over the liquid level. The copper plates mentioned previously were put into half of the flasks prepared, five plates per each. The other half of the flasks, filled only with the diesel oil under test, were left as "reference samples". The test sample sets thus prepared were

divided into two groups, each of them consisting of 4 sets with the diesel oil and copper plates and 4 sets kept as the reference sample.

The tests of the influence of copper on the oxidation stability of diesel oil with FAME content were carried out in two series. In the first one, the first group of the test sample sets was kept for a period of up to 4 weeks at a temperature of 12 °C. In the second series of tests, the storage temperature was raised to 30 °C, with maintaining the same times of exposure. The temperatures were so selected that the variations in the conditions likely to occur at e.g. filling stations depending on the season were taken into account. During the storage, the oil samples were agitated every day. Every seven days, two test sample sets, i.e. one with a copper plate placed in the diesel oil under test and one with the diesel oil kept as a reference sample, were removed from the store. The oil taken from the sample sets was then subjected to tests in accordance with the method and procedure described hereafter.

2.3. Analytical methods used

2.3.1. Determining the oxidation stability

The oxidation stability was determined with the use of three methods: conductometric test, rapid small-scale oxidation test (RSSOT), and gravimetric test.

The determination of the oxidation stability by the conductometric method was carried out in compliance with Polish Standard PN-EN 15751 [9] with the use of a METROHM Rancimat 873 instrument. In this test, a stream of cleaned and dried air was passed with a flow rate of 10 dm³/h through a diesel oil sample having been heated to a temperature of 110 °C. During the oxidation process that takes place in the fuel, volatile compounds (carboxylic acids) are formed, which flow with the air to a measuring vessel containing distilled water and provided with a conductivity cell (an electrode for the measurements of specific conductance). The volatile compounds are absorbed in water, where they dissociate, causing an increase in the specific conductance recorded by the instrument. Based on the time that elapsed to the instant of rapid growth in the conductivity, the induction period [h] was determined [9, 14].

The determination of the oxidation stability by means of the rapid small-scale oxidation test (RSSOT) was carried out with the use of a PetroOXY instrument manufactured by PETROTEST, in compliance with Polish Standard PN-EN 16091 [10]. The diesel oil sample under test was placed in a pressurized test chamber, which was then hermetically sealed. Afterwards, the chamber was filled with oxygen to a pressure of 700 kPa ± 5 kPa and heated to a temperature of 140 °C. From the instant of achieving the required temperature level, the apparatus recorded the pressure in the test chamber in 1 s intervals. As the test result, the time was recorded that elapsed from the beginning of the test, i.e. from the instant of the temperature of 140 °C being achieved by the oil sample, to the instant of a 10% drop in the pressure in the test chamber [10, 13].

The determination of the oxidation stability by the gravimetric method was carried out in compliance with Polish Standard PN-ISO 12205 [8]. Pursuant to the standard procedure,

the fuel sample was subjected to ageing at a temperature of 95 °C for 16 h, with simultaneous oxygen flow through the sample. After the ageing, the sample was filtered in order to determine the amount of insoluble filterable sediments in the oil. Additionally, sticking sediments were removed from the test tubes with the use of a three-component solvent. The result of this test was the total amount of insoluble sediments, i.e. a sum of the insoluble sticking sediments and the insoluble filterable sediments, contained in the oil and specified in g/m³ [8, 13].

2.3.2. Determining the copper content of the fuel

To determine the effect of the material-fuel interaction, the elemental copper content of some of the diesel oil samples was determined at the beginning and end of the tests. The copper content was determined in compliance with ASTM D 5185-09 by Inductively Coupled Plasma / Optical Emission Spectrometry (ICP-OES) [1].

The test methods used and the time schedule of the determinations carried out have been presented in Table 3.

Table 3. Test methods used

Parameter	Test method	Week				
		0	1	2	3	4
Oxidation stability, by the conductometric method (Rancimat)	PN-EN 15751	+	+	+	+	+
Oxidation stability, by the rapid small-scale oxidation test (RSSOT – PetroOXY)	PN-EN 16091	+	+	+	+	+
Oxidation stability, by the gravimetric method	PN-EN ISO 12205	+				+
Copper content	ASTM D 5185-09	+				+

Additionally, the state of copper plate surfaces was visually inspected after the tests.

3. Results and discussion

3.1. Changes in the oxidation stability, determined by means of the Rancimat test

Results of determining the oxidation stability of the diesel oil samples that were and were not in contact with the copper plates and were kept at two different storage temperatures (Rancimat test) have been presented in Fig. 1.

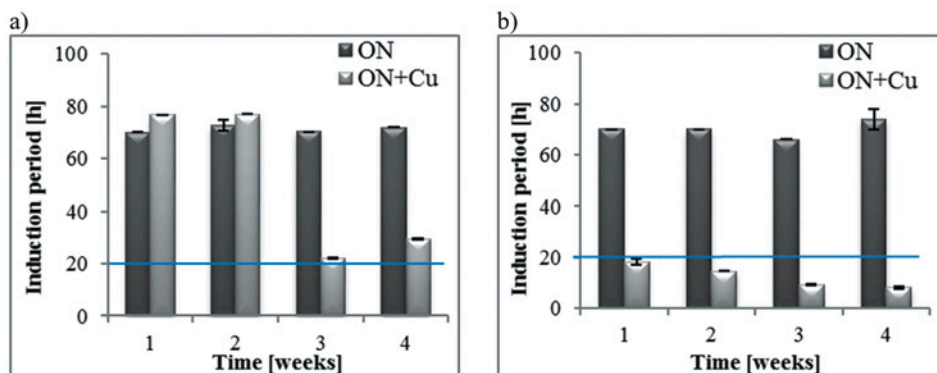


Fig. 1. Changes in the induction period (the Rancimat test) for the diesel oil samples that were and were not exposed to contact with the copper plates and were kept at a temperature of: a) 12 °C; b) 30 °C; ON – diesel oil; Cu – copper plates

At the 12 °C storage temperature, no considerable copper impact on the parameter monitored was noticed for the first two weeks (Fig. 1a). The induction period determined for the ON+Cu (diesel oil + copper plates) sample sets was comparable with that for the reference sample. The samples had to be stored for as long as 3 weeks until a drop was observed in the oxidation stability of the diesel oil exposed to contact with copper; for the sample sets without copper, the oxidation stability was not reduced at all. Although the induction period was significantly reduced for the oil-copper sample sets (by about 42 h), these samples still met the quality requirements specified for this parameter in the Regulation of the Minister of Economy [12].

At the 30 °C storage temperature, the resistance of diesel oil to oxidation in the oil-copper sample sets dropped as early as in the first week below the 20 h limit specified in the PN-EN 590 Standard and in the Minister's Regulation on the quality requirements for liquid fuels (Fig. 1b). In the next weeks, further drops in the length of the induction period were recorded for the oil-copper sets, although the drops were not as significant as observed in the first week. For comparison, no such changes were observed for the reference samples.

3.2. Changes in the resistance to oxidation, determined by means of the RSSOT – PetroOXY method

Results of determining the resistance to oxidation of the sample sets under test by the RSSOT – PetroOXY method have been presented in Fig. 2.

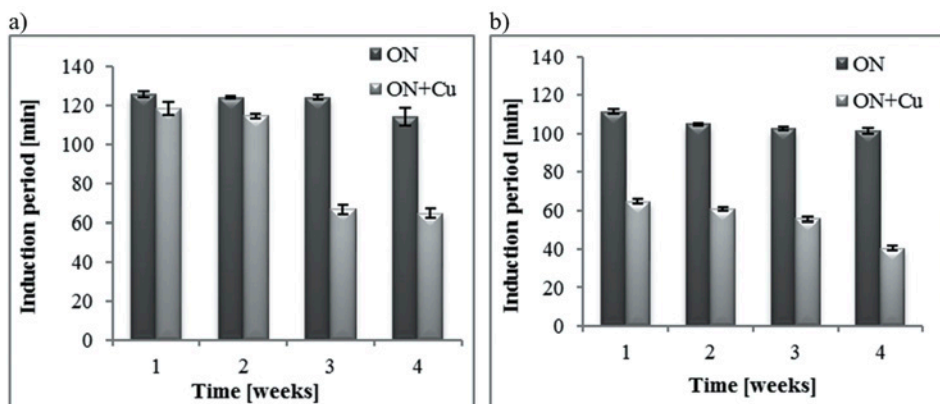


Fig. 2. Changes in the induction period (the PetroOXY method) for the diesel oil samples that were and were not exposed to contact with the copper plates and were kept at a temperature of: a) 12 °C; b) 30 °C; ON – diesel oil; Cu – copper plates

The results obtained are consistent with the results of determining the induction period by the Rancimat method. In the PetroOXY test with the oil-copper sets stored at a temperature of 12 °C, the induction period was found to drop from 120 min to 65 min in the third week of the experiment. No considerable changes were observed for the reference samples. The raising of the temperature of storage of the oil-copper sets to 30 °C resulted in a drop in the induction period length by about 50% (in comparison with the sample sets without copper) as early as after the first week of storage. In the next weeks, further drops in the value of the parameter under determination were recorded for the oil-copper sets, although the drops were not so significant.

3.3. Insoluble sediments total

The total contents of insoluble sediments in the diesel oil (ON) samples and in the oil-copper (ON+Cu) sample sets tested after four-week storage at temperatures 12 °C and 30 °C were determined in compliance with the method described in item 2.3 and the test results have been presented in Table 4.

Table 4. Insoluble sediments total

Week	Storage temperature [°C]	Insoluble sediments total [g/m ³]	
		Diesel oil (ON)	Oil-copper (ON+Cu)
0	-	8	-
4	12	9	24
4	30	11	18

For pure diesel oil, a slight increase in the total insoluble sediments content after 4-week storage was only observed in the case of the 30 °C storage temperature (a growth by 3 g/m³).

A growth in the total insoluble sediments content was recorded for the diesel oil samples exposed to contact with copper, both at the 12 °C and 30 °C storage temperature values. Noteworthy is the fact that the value of the insoluble sediments total determined for the latter storage temperature was somewhat lower than that measured for the sample sets stored at 12 °C, although higher drops in the length of the induction period were recorded for the higher temperature value. This contradiction may indicate a change in the nature of the chemical compounds being formed. Perhaps the sediments that are formed at 30 °C are washed out by the solvent used for the determination of this parameter. For this hypothesis to be confirmed, additional tests are needed. Pursuant to the requirements of the Regulation of the Minister of Economy [12], the oxidation stability of commercial diesel oil should not exceed 25 g/m³. The sample sets under test were in conformity with this requirement, but attention should be paid to the fact that the test results obtained are close to the said maximum acceptable value.

3.4. Copper content of the fuel

The elemental copper content of the diesel oil under test was determined with the use of the Inductively Coupled Plasma / Optical Emission Spectrometry (ICP-OES) technique. The tests were carried out on diesel oil samples stored for a period of 4 weeks and the test results have been specified in Table 5.

Table 5. Copper content of the fuel under test after a 4-week storage period

Sample	Diesel oil (ON)	Oil-copper (ON+Cu), 12 °C	Oil-copper (ON+Cu), 30 °C
Copper content [mg/kg]	< 0.1	0.2	0.4

In the oil-copper sample sets, a growth in the copper content of the diesel oil under test was recorded. This has confirmed the occurrence of interactions between copper and diesel oil. With a growth in the storage temperature, while the time of the diesel oil exposure to contact with copper remained unchanged, the copper content of the fuel increased. The accelerating or inhibiting impact of copper on the fuel depends on the concentration of copper ions in the fuel. If this concentration is lower than 250 ppm, then the inhibiting impact of the copper ions is assumed to predominate.

3.5. Macroscopic visual assessment of the copper plates used

The appearance of the copper plates after 4-week storage in diesel oil at temperatures of 12 °C and 30 °C has been presented in Fig. 3.

Colour changes and solid reaction products were found to appear on the copper plate surfaces. The changes were bigger for the plates kept in the diesel oil at higher temperatures. The visual observations were consistent and confirmed the results obtained from the oxidation stability tests.



Fig. 3. The appearance of the copper plates before and after the exposure to contact with the diesel oil

4. Conclusions

The experiments carried out have shown that copper interacts with commercial diesel oil and adversely affects the oxidation stability of the oil and this confirms the literature reports on the catalytic influence of copper compounds on the oxidation processes that take place in the fuel. Since copper is a component of the materials used for the construction of pipelines in process installations at filling stations, the copper interaction with diesel oil may be a reason for a deterioration in the quality of such a fuel and, in consequence, for a failure of this fuel to meet the standard requirements for the fuel resistance to oxidation. It should be remembered, however, that the time after which the induction period was considerably shortened, especially at lower temperatures, was relatively long (3 weeks) in comparison with the statistical period of a specific fuel batch being exposed to contact with copper parts of the process installation. On the other hand, the experiments revealed that a growth in the storage temperature by less than twenty centigrade degrees caused a much faster drop in the length of the induction period for the diesel oil being in contact with copper, which shows that not only the contact with copper but also the time of exposure to such a contact has a significant impact on the oxidation stability of the oil.

References

- [1] Astm D5185-09: Standard Test Method for Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).
- [2] Biernat K. Storage Stability of Fuels. InTech. 2015.
- [3] Clark RH. In Proceedings of the 3rd International Conference on Stability and Handling of Liquid Fuels, London, UK, 13-16 Sept. 1988: 283.
- [4] Fuels and Lubricants Handbook. Astm. 2003.
- [5] Groysman A. Corrosion for Everybody. Springer. 2010.
- [6] Jakóbiec J, Ambrozik A. Procesy starzenia estrów metylowych kwasów tłuszczowych oleju rzepakowego (Ageing processes of rape-seed oil fatty acid methyl esters). Inżynieria Rolnicza. 5(114)/2009.
- [7] Marek A, Hefczyk B, Stec Z. Badania szybkości inicjowania procesów wolnorodnikowych wybranymi inicjatorami (Investigation on the rate of initiation of free-radical processes by selected initiators). Proceedings of the Silesian University of Technology, Department of Chemical Organic Technology and Petrochemistry.
- [8] PN-ISO 12205: Oznaczanie odporności na utlenianie średnich destylatów paliwowych (Petroleum products – Determination of the oxidation stability of middle-distillate fuels).
- [9] PN-EN 15751: Paliwa do pojazdów samochodowych – Estry metylowe kwasów tłuszczowych (FAME) jako samoistne paliwo i ich mieszaniny z olejem napędowym – Oznaczanie stabilności oksydacyjnej metodą przyspieszonego utleniania (Automotive fuels. Fatty acid methyl ester (FAME) fuel and blends with diesel fuel. Determination of oxidation stability by accelerated oxidation method).
- [10] PN-EN 16091: Ciekłe przetwory naftowe – Paliwa i mieszaniny ze średnich destylatów naftowych i estrów metylowych kwasów tłuszczowych (FAME) – Oznaczanie stabilności oksydacyjnej metodą szybkiego utleniania w małej skali (Liquid petroleum products. Middle distillates and fatty acid methyl ester (FAME) fuels and blends. Determination of oxidation stability by rapid small scale oxidation method).
- [11] Pande SG, HARDY DR. The effect of copper, MDA and accelerated aging jet fuel thermal stability as measured by the gravimetric JFTOT. 5th International Conference on Stability and Handling of Liquid Fuels Rotterdam, the Netherlands. October 3-7, 1994.
- [12] Regulation of the Minister of Economy of 9 October 2015 on the quality requirements for liquid fuels (Dz. U. (Journal of Laws) of 2015, item 1680).
- [13] Sacha D. Ocena stabilności oksydacyjnej paliw do silników o zapłonie samoczynnym według projektowanych wymagań CEN (Evaluation of the oxidation stability of the fuel for compression ignition engines according to the proposed requirements of CEN). Nafta i Gaz. No. 11/2013.
- [14] Stanik W, Mazanek A, Jakóbiec J. Study of diesel oil containing 7% (v/v) of FAME and cetane boost additive for the assessment its utility and purity of injectors. Combustion Engines. 2015; 162(3): 933-943.
- [15] Walling C. Free Radicals in Solution. John Wiley and Sons. NY, USA. 1957: 427.