Dyeing and marking system in European Union and Poland

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Introduction

In September last year 10 years had passed from the introduction of a system of marking by Solvent Yellow 124 of fuel, which has lower duty on the Polish market. Polish law has been modified a few times and adjusted to European Union requirements. Poland as an EU member with full rights can actively participate in the next verification of EU decision in this field.

European law in this field

Markers and dyes are used in order to distinguish fuels with different tax, especially when the properties of these fuels are very similar. A marker does not change the natural color of fuel and it can be detected by the very simple chemical test, however a dye gives fuel a color in order to visually distinguish it.

As a marker is used the substance, which is named N-ethyl-N-[2-(I-isobuthoxyethoxy)ethyl]-4- (phenylazo)aniline. This substance is used in all over the EU and commonly named as a euromarker (Solvent Yellow 124).

The first decision in the matter of creating common rules of marking fuel with lower tax was written in Directive 95/60/EC dated 27th November 1995. This Directive introduced the possibility of diesel and kerosene marking, and it did not define the name of chemical compound, which could be used as a marker. The marker would have been chosen after testing. During choosing this product following properties were taken into consideration as solubility in petroleum products, physical and chemical stability, influence on health and the environment, resistance to removing and cost of detection. Research was conducted in Joint Research Centre and in 14 laboratories of EU Members. From among several tested substances the best opinion received Solvent Yellow 124 and just it was appointed in the European Commission decision 2001/574/EC dated 13th July 2001 as the common fiscal marker. This decision announced, that SY 124 would be introduced to be used from the 1st September 2002, and the level of marking established from 6 mg/l.

As a result planned revision and verification of the above regulations following decision 2003/900/EC dated 17^{th} December 2003 appointed a maximum level of marking as 9 mg/l, motivating this decision by the need for calculating false usage of marking fuels. The last decision – 2006/428/ EC dated 22^{nd} June 2006 edited after further consultations, conducted by every EU Member, maintained earlier settlements.

EU Members can use their own system of color distinguishing of products (in Table I shows dyes used in several selected countries in EU). **Table I**

Make use of dyes for tax fuel in 15 countries of th

Country	Product	Dye Marker System (post August 2002)	Dye con- tent
Austria	gas oil	red dye	visible
Belgium	heating oil	red dye	visible
Denmark	gas oil	Solvent Blue 35	5.0 mg/l
Finland	gas oil	Solvent Red 19	3.0 mg/l
France	gas oil marine diesel	Solvent Red 24 Solvent Blue 35	10.0 mg/l 10.0 mg/l
Germany	gas oil	Solvent Red 19	5.0 mg/kg
Greece	gas oil	red dye	visible
Holland	heating oil	red dye	visible
lris	gas oil	Solvent Blue 35	5.0 mg/l
Republic	kerosene	Solvent Red 19	3.0 mg/l

Country	Product	Dye Marker System (post August 2002)	Dye con- tent
Italy	gas oil	Solvent Green 33	5.0 mg/l
Luxem- bourg	heating oil	red dye	visible
Portugal	gas oil (agriculture)	Solvent Blue 35	5.0 mg/l
	gas oil (heating)	Solvent Red 19	4.2 mg/l
Spain	gas oil (type B- agri-	red dye	min abs 0.4
	culture) gas oil (type C		
	-heating)	blue dye	min abs 0.5
Sweden	gas oil	Solvent Blue 35	5.0 mg/l
United	gas oil	quinizarin	1.75 mg/l
Kingdom	kerosene	coumarine	2.20 mg/l

Polish law in this field

In Poland dyeing red heating oils was introduced in August 1998. In September 1999 in addition to dyeing, the obligation of marking was also introduced. In the ordinance [2] was published the chemical name of using marker (N-Ethyl-N-[2-(1-isobutoxyethoxy)ethyl]-4-(phenylazo) aniline, the catalog name Solvent Yellow 124 and minimal level of dozing of the marker 5,4 mg/kg of heating oil.

The next ordinance dated 22^{nd} March 2002 [3] changed the level of marker dozing (not less than 4.6 mg/l) and announced catalog names of two dyes allowed for fuel dyeing: Solvent Red 164 (not less than 6.6 mg/l) and Solvent Red 19 (not less than 6.3 mg/l).

The ordinance dated 17^{th} December 2002 [4] introduced the following changes: concentration of marker fixed on a level not lower than 6.0 mg/l, and dyes defined as substances type Solvent Red 164 and type Solvent Red 19.

The ordinance dated 30^{th} May 2005 [5] introduced an additional obligation of marking and dyeing of shipping fuel. It was determined, that for marking marker Solvent Yellow 124 should be used, and for dyeing – dye type Solvent Blue 35.

The last ordinance by the Finance Ministry dated 12th February 2009 [6] defined maximum and minimum limits of marker concentration in fuel. The proper marked product should contain not lower than 6.0 mg/l and not more than 9,0 mg/l of marker SY 124. Heating oil can be dyed red with dye SR 19 to the amount not less than 6.3 mg/l or with dye SR 164 to the amount not less than 6.6 mg/l. Shipping fuel shall be dyed green with SB 35 with the amount not less than 6.0 mg/l. In comparison with previous ordinance dated 30th May 2005 the names of dyes are not preceded by the word "type".

In practice, for different reasons, economic, ecological or technological, fuel producers to dye their products use chemical compounds, which are not precisely the dyes SR 19 and SB 35 mentioned in ordinance dated 12th February 2009. These compounds are sometimes even mixtures of several compounds, described as the substitutes of SR 19 and SB 35. The producers of the substitutes describe them also as the names "SR 19 type" or "SB 35 type". Spectral characteristics in the visible light of the substitutes allows selection of the analytical wave length (it means this, for which absorbance is maximum) identical as for neat dyes SR 19 and SB 35. This dependence was used for the quality determination of them in the finished product.

Dyeing and marking of the fuels happens by adding the right amount of package containing the marker SY 124 and the required substitute of dye. These components are dissolved in an organic carrier. Proportion between amount SY 124 and dye are determined by the producer of the package.

Analysis of the quantitative composition available on the Polish market packages and last ordinance requirements shows, those producers can have large difficulties in proper marking and dyeing of fuels produced by them. At first for the reason of the entry in the last ordinance, which after crossing the word "type" before the name of the dye practically does not allow usage of the substitutes; the second, for the reason of the incoherent proportion between the amount of SY 124 and dye in the market package and entries in the ordinance.

Besides the marking and dyeing process of some kinds of fuel, the process of the proper determination of individual dyes and markers in the laboratories is very important.

Incoherent requirements of the ordinance with the real process of the fuel dyeing with dyes "SR 19 type" and "SB 35 type" may cause laboratories problems with proper determination of the amount of two dyes. Measuring mistakes and incorrect interpretation of the received results are often reflected in problems with correct taxation of the product.

The ordinance dated 12^{th} 2009 [6] states dyeing of the heating oil with dye SR 19, and shipping fuel with dye SB 35, so in fuels one should determine the exact concentration of these dyes, not their substitute.

In research methods (e.g. DIN 51 426 [7]) applying to determine the SR 19 amount as the standard substance is used the compound trade name Sudan Red 7B (Solvent Red 19 in powder). On the other hand, as mentioned earlier, in reality in the fuel is the substitute of this dye, in other words, dye Solvent Red 19 type. If we prepare two solutions of identical concentration of dye SR 19 and SR 19 type (10 mg/l), then we analyze them with a spectrophotometer in visible light range, we received spectrum as shown in Picture I. The upper limit shows absorbance of the standard solution of SR 19, and lower limit - absorbance of the substitute (SR 19 type). Maximum absorbance occurs in both cases at wave length 540 nm and gives, respectively: 0.826 and 0.608. The difference is considerable and it influences the finishing result of the determination. Summarizing: if the heating oil will be dyed with the package, which contains dye SR 19 type, and in the laboratory as the standard to determine the dye content in fuel, the compound Sudan Red 7B (Solvent Red 19) will be used, the determined concentration of the dye SR type will be lower in the relation to the real, dosed amount.

In the research methods used to determination the amount of dye SB 35 as standard substance the compound of the trade name of Sudan Blue II, known also as Solvent Blue 35, is used. It is available on the market only in a neat form and it has quality certification. On the market there are two dyeing packages, which contain substitutes of dye SB 35 and they are named dye SB 35 type.



Fig. 1. Comparison of the spectrum of Solvent Red 19 and Solvent Red 19 type

If we prepare three solutions, the first containing the standard of the dye SB 35, the second – the trade package No. I, and the third – trade package No. 2, all solutions have the same concentration, and we do an analysis with the spectrophotometer in the visible light range, we receive the spectrum as in the Picture 2. Maximum absorbance is at all cases for the wave length 650 nm and gives respectively: 0.498; 0.299; 0.499. As can be seen, absorbance for the dye contained in the package no I is the same as for the standard, however absorbance for the dye contained in the package No. 2 is lower, what as mentioned earlier, influences the finished result of the measurement. The substitute of dye

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SB35, contained in the package No. 1, is the equivalent of the standard dye and in this case there will not be problems with correct, quantitative determination of this substance in the fuel, however for the package No. 2 the mistakes of the determination will be significant.

In the case, when an independent laboratory receives a test sample of the fuel, it either receives correct results or considerably lowers in comparison with the real dosed amount of the dye. It will be dependent on which package will be used to dye the fuel. Then one result will meet the requirements [6], the second will be on the limit of the requirements.



Fig. 2. Comparison of the spectrum of Solvent Blue 35 type and Solvent Blue 35 colour equivalent

Summary

Correct determination of the content of the marker and dyes is very important for the proper taxation of the fuel. Explicit interpretation of the requirements is essential because:

- producers could correctly dye and marker their products
- independent analytical laboratories could correctly determine content two components in fuel.

Laboratories must be sure, that they determine the content of dye SR 19 and SB 35, not their substitutes, and fuel producers must know, that every laboratory determines dye SR 19 and SB 35, not their substitutes. In the light of this the last and the next to the last ordinance of Finance Ministry [5,6] it seems, that there will be large difficulties with this.

Literature

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English translation by the Author

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- 3. Dziennik Ustaw nr 27 z 2002 r., poz. 269.
- 4. Dziennik Ustaw nr 216 z 2002 r., poz. 1829.
- 5. Dziennik Ustaw nr 97 z 2005 r., poz. 815.
- 6. Dziennik Ustaw nr 32 z 2009 r., poz. 218.
- 7. DIN 51 426:2002: Spektrofotometryczne oznaczanie zawartości czerwonego barwnika i markera-2 w lekkim oleju opałowym.

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