CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 8, No. 2, 2014 Chemical Technology

Ivanna Saban, Oleg Grynyshyn and Victoria Kochubei

PHYSICO-CHEMICAL CHARACTERISTICS AND THERMAL STABILITY OF OIL BASED LUBRICATING FLUIDS FOR GLASSWARE PRODUCTION

Lviv Polytechnic National University,
12, St. Bandera str., 79013 Lviv, Ukraine

Received: September 11, 2013 / Revised: September 21, 2013 / Accepted: November 12, 2013

Abstract. The investigation results about physico-chemical characteristics of I-40 and MS-20 commercial mineral oils are represented. It is shown that such oils may be the basis for the lubricating fluids used for press mold lubrication while glass containers production. Thermal stability of oils and their hydrocarbon fractions was studied. It was established that I-40 oil contains resins capable to form coke-like densification products while their burning. It is recommended to use MS-20 oil as the basis for lubricants.

Keywords: lubricant, oil basis, press mold.

1. Introduction

It is well-known that glass containers are widely used in various branches of industry and life because they are comfortable, safe, cheap, environmentally friendly and chemically resistant. The glass containers are produced at the temperatures higher than 723 K in the special metal molds *via* pressing.

Lubrication of metal molds is an important stage of the production. Information about interaction "glass -oil-metal" allows to optimize this stage [1]. Lubricating fluids should be effective under any conditions and provide the process continuity. Machines for glassware production demand oils with wide temperature working range and capability of evaporation without deposits. At the same time they should prevent formation of defects, scratches, glass adhesion to metal and should not cause metal oxidation. Ukraine does not produce such lubricants and has to buy these expensive products abroad. Therefore the development of effective domestic lubricating fluids is the urgent problem.

Nowadays black-lead lubricants are the most widely used materials for glassware production. Many reports represent their assortment, composition and production technology [2, 3]. However, these lubricants have a series of disadvantages: insufficient lubricating-cooling properties, high specific consumption, pollution of the working zone by decomposition products, graphite deposition while storage.

We propose to use hydrocarbon lubricating fluids on the basis of oils. The diluent regulating the colloidal structure, as well as thickener promoting the formation of thick film between mold and hot glass are also the parts of lubricants. The quality of lubricating fluid to the greatest extent depends on oil basis. Therefore it is very important to make the best choice.

There is a series of technical and sanitary requirements for the oil bases. The technological requirements are: good lubricating properties, low gas forming ability, good evaporation without the formation of deposits, low cost, availability. Glass companies assess environmental safety of production, control and eliminate pollution of the environment and working area [4]. Therefore the toxic properties of oil basis, as well as its explosive and fire safety are extremely important. The nature of the toxic effect of oil basis depends on its chemical composition and depth of treatment.

However, the most important properties of oil basis that actually determine the operational properties of lubricating fluids are viscosity-temperature properties and thermooxidation resistance. Minimal carbon formation on the working surfaces and change in viscosity of oil basis when changing the temperature will ensure the effective operation of lubricating fluids and operational reliability of glass forming equipment. Running ability is mainly determined by the initial composition of oil fractions, including the content of paraffinic, naphthenic and aromatic hydrocarbons [5].

2. Experimental

When selecting objects of study we took into account the impact of the hydrocarbons fraction structure on the oils quality, as well as their availability and low cost.

The analysis of commercial mineral oils produced by oil refining industry of Ukraine was carried out. Thus we selected the following oils to study their possible use as a base component for the production of lubricants:

- Aeroengine oil MS-20.
- Industrial oil I-40.

For the selected oils we determined density using a pycnometric method, the refractive index using a refractometer, the molecular mass using a cryoscopy, viscosity at 323 and 373 K using a viskosimetry, flash point, ash content and coke forming ability [6]. Ring analysis by the standard *n-d-M* method [6] was carried out as well.

Group hydrocarbon composition of oils was studied by a chromatographic method. Silica gel of ASK mark was used as an adsorbent. The length of chromatographic column was 1600 mm, diameter 15 mm. The column was loaded by 200 g silica gel, previously dried at 573 K in a muffle furnace. Oil sample was diluted with the petroleum ether in the ratio of 1:3. Hydrocarbon fractions were washed out by the petroleum ether and benzene, and resins were desorbed by the alcohol-benzene mixture [6]. Then physical and chemical parameters were determined for specific groups of hydrocarbon fractions.

Investigations of thermal stability were carried out using Q-1500D derivatograph of "Paulik-Paulik-Erde" system with the computer recording of the analytical signal mass loss and thermal effects. Samples were analyzed at the heating rate of 10°/min in the air under a dynamic mode. The samples mass was 100 mg. Aluminum oxide was the reference substance.

3. Results and Discussion

As it was mentioned above, the physico-chemical properties of oil have a decisive impact on the running ability of lubricating fluids (Tables 1 and 2).

Paraffin-naphthenic hydrocarbons were the basis of both oils. The presence of small quantities of resins (0.53 wt %) is typical for I-40 industrial oil. It is expected that resins will cause the excessive coke forming on a hot metal surface of the lubricated mold.

Table 1

Physico-chemical characteristics of commercial oils

Index	I-40	MS-20
Physico-chemical charactersitics		
Density, r_4^{20}, g/cm^3	0.8957	0.8935
Molecular mass	345	535
Refraction index, n_D^{20}	1.4919	1.4938
Viscosity, mm^2/s,		
at 323 K	41.95	131.23
373 K	8.56	24.28
Flash point (open device), K	477	505
Coke forming ability	0.20	0.19
Ash content	0	0
Structural-group composition by *n-d-M* method		
Carbon content in aromatic rings, % C_a	14.26	6.04
Carbon content in naphthenic rings, % C_n	32.11	32.99
Carbon content in paraffinic chains, % C_p	53.63	60.97
Number of aromatic rings in the molecule, K_a	0.60	0.40
Number of naphthenic rings in the molecule, K_{n}	1.80	2.87
Hydrocarbon group composition, mas %		
Paraffin-naphthenic, n_D^{20} till 1.49	67.19	77.75
Aromatic monocyclic, n_D^{20} = 1.49–1.53	25.3	16.98
Aromatic bicyclic, n_D^{20} = 1.53–1.59	4.41	4.55
Aromatic bicyclic n_D^{20} > 1.59	2.57	0.72
Asphaltic-resinous compounds	0.53	–

Table 2

Physico-chemical characteristics of the group hydrocarbon fractions

Index	I-40				MS-20			
	Paraffin-naphthenic	Mono-aromatic	Bi-aromatic	Poly-aromatic	Paraffin-naphthenic	Mono-aromatic	Bi-aromatic	Poly-aromatic
Density, r_4^{20}, g/cm^3	0.8882	0.9043	-	-	0.8731	0.9005	-	-
Refraction index, n_D^{20}	1.4858	1.5112	1.5420	1.5920	1.4820	1.5040	1.5640	1.6118
Viscosity, mm^2/s, at 323 K	34.30	51.32	-	-	125.43	132.46	-	-
373 K	7.78	8.52	-	-	23.87	25.12	-	-

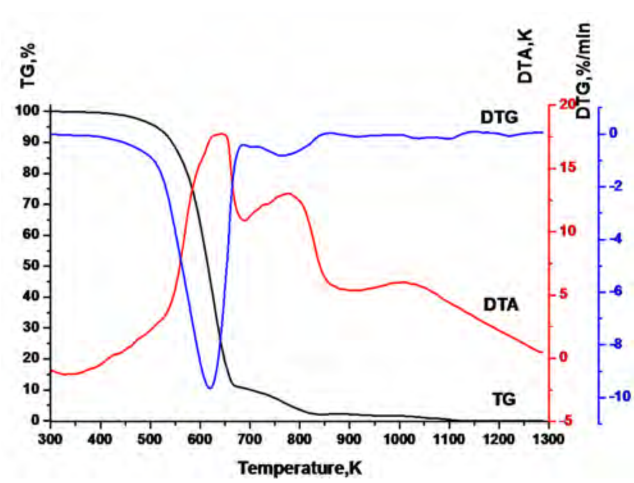

Fig. 1. Thermogram of I-40 oil

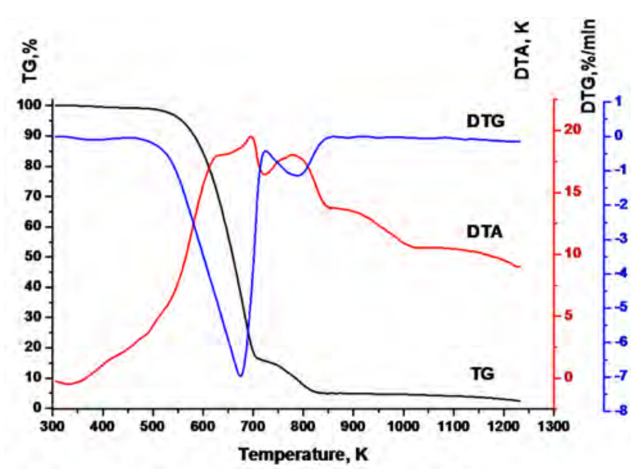

Fig. 2. Thermogram of MS-20 oil

Table 3

Thermal investigations of MS-20 oil and its group hydrocarbon fractions

Fraction	Stage	Temperature range, K	Mass loss, %	Maximum effect at the temperature of, K
Paraffin-naphthenic	I	443–719	90.0	671
	II	719–781	9.6	780
Monoaromatic	I	483–729	84.5	651; 687
	II	729–855	11.7	753
Biaromatic	I	523–738	80.4	701
	II	738–910	17.8	809
Polyaromatic	I	525–745	83.0	688
	II	745–900	14.3	753; 820
Oil MS-20	I	487–721	83.2	630; 694
	II	721–856	10.8	780

Table 4

Thermal investigations of I-40 oil and its group hydrocarbon fractions

Fraction	Stage	Temperature range, K	Mass loss, %	Maximum effect at the temperature of, K
Paraffin-naphthenic	I	435–655	86.5	635
	II	655–821	10.9	754
Monoaromatic	I	474–695	91.1	633; 671
	II	695–860	8.9	781
Biaromatic	I	478–733	77.3	675
	II	733–909	22.7	835
Polyaromatic	I	482–761	74.0	678
	II	761–948	26.0	841
Oil I-40	I	444–687	89.3	641
	II	687–893	8.5	776

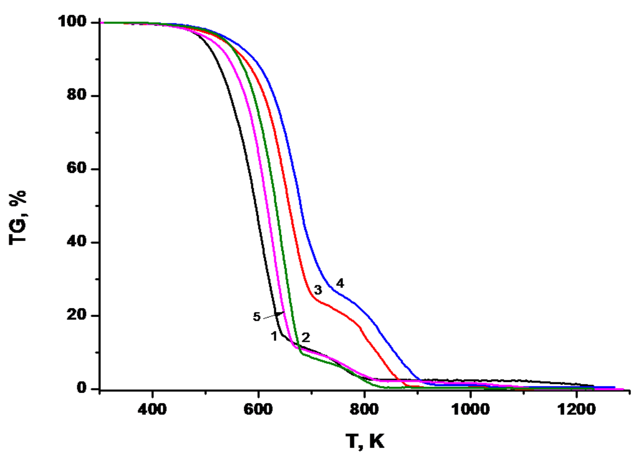

Fig. 3. TG curves of I-40 oil (5) and its group hydrocarbon fractions: paraffin-naphthenic (1); monoaromatic (2); biaromatic (3) and polyaromatic (4)

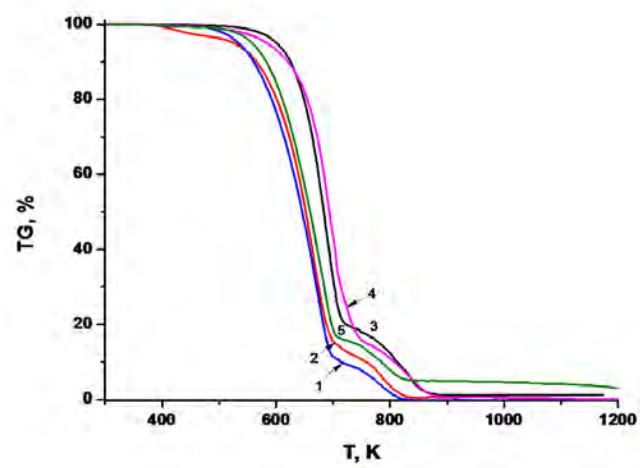

Fig. 4. TG curves of MS-20 oil (5)and its group hydrocarbon fractions: paraffin-naphthenic (1); monoaromatic (2); biaromatic (3) and polyaromatic (4)

Resistance to oxidation, thermal stability, viscosity-temperature properties and carcinogenicity of oils depend on the content of aromatic hydrocarbons in them.

The oils of the same group composition but different viscosity have different influence on the processing characteristics of lubricating fluids. In particular, the increase of viscosity increases the lubricating ability but also increases the ability to carbon formation. The presence of great quantity of light fractions results in the smoke and oil fog formation that worsens the working climate.

The increase of oils molecular mass increases their lubricating ability but decreases dispersion and increases the thickness of the lubricating film. As a result, the consumption of the lubricating fluid increases.

Thus, from the point of view of physico-chemical properties, structural-group and hydrocarbon group composition the oils I-40 and MS-20 may be used for the lubrication fluids production.

While contacting with the hot glass oil undergoes physical and chemical changes, such as evaporation, thermal destruction, densification and deep oxidation followed by the formation of the complete and incomplete burning products. Therefore the thermal stability is one of the main demands for oil basis. Tables 3 and 4 represent results of oil and group hydrocarbon fractions thermolysis. Thermograms of the samples are given in Figs. 1 and 2. The results of thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) show that thermolysis of I-40 and MS-20 oils proceeds during two stages. The first stage of MS-20 oil thermolysis is observed in the range of 443–746 K (Table 3) and for I-40 – in the range of 435–761 K (Table 4). At this stage all samples loss their main mass due to the thermooxidative destruction of hydrocarbons and their partial burning. The stage is accompanied by the appearance of the first considerable exothermal effect observed on DTA curves.

The second stage of MS-20 oil thermolysis is observed in the range of 719–910 K (Table 3) and for I-40 – in the range of 655–948 K, where the pyrolytic residuals of the samples are burned. This stage is accompanied by the appearance of the second exo-effect.

Thermogravimetric curves of both oils are represented in Figs. 3 and 4. The least thermal stability is observed for paraffin-naphthenic hydrocarbons. The temperature intervals of the first and second stages of their thermolysis are shifted to the area of low temperatures. The maxima of exothermal effect of this hydrocarbon fraction are observed at lower temperatures compared with other hydrocarbon fractions (Tables 3 and 4). While heating these hydrocarbons loss their masses more intensively compared with other fractions (Figs. 3 and 4).

The highest thermal stability is observed for bi- and polycyclic aromatic fractions. The temperature intervals and maxima of exo-effects are shifted to the area of high temperatures. While heating these fractions loss their masses with the least intensity.

The samples of the initial I-40 and MS-20 oils have the medium thermal stability compared with their group hydrocarbon fractions. Temperature intervals and maxima of exothermal effects of thermooxidative destruction of I-40 and its fractions are shifted to the area of lower temperatures compared with MS-20 and corresponding hydrocarbon fractions (Tables 3 and 4).

In contrast to MS-20, the thermal stability of I-40 oil is higher. MS-20 losses its mass during heating less intensively. It is obvious from the results represented in Tables 3 and 4. Temperature interval of its thermooxidative destruction shifts toward the area of high temperatures. The similar thermal stability is typical of definite hydrocarbon fractions in its composition. The high thermal stability of MS-20 oil ensures lower gas formation during lubricant usage and improves sanitation conditions at the enterprise.

4. Conclusions

On the basis of obtained results about physico-chemical properties of commercial oils produced at Ukrainian refineries, as well as their structural and group composition, we recommended MS-20 as the oil basis of lubricating fluids for glassware production. Since I-40 oil contains asphalto-gumming substances, densification products will be formed on the mold surface and thus operating properties of lubricating fluid will be worse. The results of thermal analysis demonstrate that MS-20 oil and its hydrocarbons have higher thermal stability compared with that of I-40 oil and its hydrocarbon fractions. Taking this fact into account the ecological indexes of technological lubricant will be better.

References

[1] Papsheva E.: Verre, 2009, **15**, 38.
[2] Kargin B., Diamantopulo K., Ryzhenina A. and Lavrenshina A.: Mir Techniki i Techn., 2009, **10**, 20.
[3] Khamidov B., Ismailov M. and Saidakhmetov Sh.: Konf. “Nefteperarobtka i Neftekhimiya”, Bashkortostan, Ufa 2003, 142.
[4] Trifonova T. and Ishunkina N.: Steklo i Keramika, 2007, **6**, 32.
[5] Yasinenko E., Sokolov A. and Levanova S.: 12 Mezhd. Konf. “Naukoemkie Khim. Techn.”, Russia, Volgograd 2008, 41.
[6] Isaguliants V. and Egorova G.: Khimiya Nefti. Khimiya, Moskwa 1965.

ФІЗИКО-ХІМІЧНІ ХАРАКТЕРИСТИКИ І ТЕРМІЧНА СТАБІЛЬНІСТЬ ОЛИВНИХ ОСНОВ МАСТИЛЬНИХ РІДИН ДЛЯ ВИРОБНИЦТВА ВИРОБІВ ІЗ СКЛА

Анотація. *Наведено результати досліджень фізико-хімічних характеристик товарних мінеральних олив І-40 та МС-20, які можуть слугувати оливною основою мастильних рідин для змащення прес-форм у процесах виробництва склотари. Досліджено термічну стабільність олив та їх груп вуглеводнів. Встановлено, що олива І-40 містить смолисті речовини, які в процесах згорання будуть утворювати коксоподібні продукти ущільнення. Рекомендовано основою мастильних рідин використовувати оливу МС-20.*

Ключові слова: *мастильна рідина, оливна основа.*