

Recovery of silver from zinc cakes

B. I. Lucheva*, P. K. Iliev, Vl. P. Stefanova

Department of Non-ferrous Metals, University of Chemical Technology and Metallurgy, Sofia 1718, Bulgaria

Received June 27, 2014; Accepted April 8, 2015

The present experimental study investigates the feasibility of thiosulfate recovery of silver from zinc cakes produced in the process of wet recovery of zinc cakes at the KCM Ltd in Bulgaria. The impact of various factors on the rate of silver recovery through thiosulfate leaching is studied. It is found that the rate of silver recovery is 70-74 % within the temperature range of 30-50°C at 20% pulp density and leaching time of 30 min, irrespective of the solution pH. The behavior of copper, lead, zinc and iron during thiosulfate extraction is also observed. The thiosulfate solution pH is maintained to 7-8 in order to reduce by hydrolyzation the concentration of the metals that have been transferred to the solution except silver. After subsequent precipitation of the silver by means of Na₂S, silver concentrate is produced. The possibility of regeneration of the thiosulfate solution is discussed. The solid residue from thiosulfate leaching contains 10-40 g/t silver and can be processed by a Waelz process.

Keywords: zinc cake, silver, thiosulfate leaching.

1. INTRODUCTION

The wet recovery of zinc by the technology adopted at KCM Ltd in Bulgaria takes place at relatively low acidity of the solution without bringing the impurities contained in the zinc concentrates into the solution. Thereupon, the metals are concentrated in the zinc cake which subsequently is subjected to Waelz-processing. After Waelz-processing the precious metals completely pass into the clinker and, due to the lack of a proper technology for their recovery they are irretrievably lost.

To prevent the loss of precious metals, attempts for their recovery from the zinc cakes are made at some plants with similar technology.

All known methods for zinc cakes processing in the world-wide practice can be divided into three groups [1]:

1. Waelz-process; reductive flash roasting; smelting in gas-generator, shaft, reverberatory, cyclone, and electric furnaces.
2. Roasting of the cakes in a mix with zinc or pyrite concentrates; treatment with SO₂ or sulfation with sulfuric acid.
3. Direct dissolution of the cakes in sulfuric acid at increased acidity and temperature.

Usually the hydrometallurgical methods of zinc cakes processing based on the reactions of ferrite decomposition using sulfuric acid at atmospheric or higher pressure have achieved greater development.

The complex composition and a large amount of very small size classes in the zinc cake make it a difficult object for leaching and flotation.

In recent years, there has been renewed interest in the use of thiosulfate as a substitute for cyanide in gold and silver leaching [2]. Many attempts have been taken for leaching silver sulfide with thiosulfate, each utilizing different additional reagents and conditions [3,4]. The cupric-ammonia catalyzed system has been the most commonly studied system because of its ability to leach gold, silver and silver sulfide.

The developed and patented hydrometallurgical method of zinc cake processing [5] is of certain interest. It is based on silver recovery by means of sodium thiosulfate in the presence of ammonium sulfate as an activator at a temperature of 30-60°C and pH=4-6. In this process, the silver passes into the solution wherefrom it is recovered by cementation with zinc powder. The solid residue is re-pulped by the same thiosulfate solution and is subjected to flotation. The drawbacks of that method are the low rate of silver recovery in the cement precipitate, its circulation in turnover with the flotation concentrate, considerable losses (over 10 %) with the clinker, as well as considerable loss of zinc in the thiosulfate solutions.

The purpose of this experimental work is to determine the behavior of silver and other metals contained in the zinc cakes at thiosulfate leaching and to investigate the feasibility of solution regeneration after precipitation of the silver by Na₂S.

* To whom correspondence should be sent.
E-mail: plasma@dir.bg

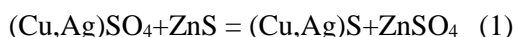
2. EXPERIMENTAL

2.1. Materials

The subject of the investigation is a zinc cake – a waste product from the wet recovery of zinc cakes at KCM Ltd. The chemical composition of the cake was determined through atomic absorption analysis as presented in Table 1.

The phase analysis of zinc cake obtained at similar plant applying the same technology for zinc cakes processing [6] shows that:

1. The zinc exists in the form of sulfate, oxide, silicate, sulfide and ferrite.
2. The lead in the cake exists in the form of anglesite (PbSO_4), cerusite (PbCO_3), galenite (PbS), plumbojarosite $\text{PbFe}(\text{SO}_4)_3(\text{OH})_{12}$.
3. The copper is a very thin (up to 3 microns) edging of sulfide Cu_2S on zinc silicate and zinc oxide grains and as isomorphic admixture in sphalerite and zinc ferrite.
4. The silver in the zinc cake is mainly contained in the crystal lattice of the secondary covelline, while part of it is adsorbed by the iron hydroxides [7]. According to the authors, in the process of recovery of the zinc cakes, the copper and silver pass into the solution, and after that their ions interact with the zinc sulfide by the reaction:



Cake, for the most part, consists of particle aggregates with size 10-15 microns. The latter contain particles to submicron size. More than 90% of the silver is concentrated in size classes less than 40 microns [6].

Upon recovery of the zinc cake with water for 1 hour at a temperature of 70°C, 3.97 % of the copper and 16.19 % of the zinc pass into the solution. The total content of water-soluble compounds in the zinc cake is 18.75 %.

For recovery of silver from the cake a sodium thiosulfate pentahydrate solution was used. Water solution of sodium sulfide was used as precipitator of the silver.

2.2. Methods

The leaching experiments for silver recovery from the cake were carried out in a thermostat in order to maintain the defined temperature. The stirring of the pulp was realized by means of a mechanical stirrer. The defined level of solution pH was reached and maintained by means of lime milk.

The silver precipitation experiments were carried out using a magnetic stirrer at room temperature. Atomic absorption analysis was used

to determine the concentration of Ag, Cu, Fe, Pb, Zn in the thiosulfate solution, the solid residue, and the sulfide concentrate.

RESULTS AND DISCUSSION

3.1. Thiosulfate recovery of silver from zinc cake

The factors influencing the rate of silver recovery by thiosulfate leaching of zinc cake are: sodium thiosulfate concentration, type and quantity of the additions which stabilize the solution, temperature, pulp density, leaching time and pH of the medium.

Thiosulfate ion is a metastable anion with a tendency to chemical decomposition in water solutions. The oxidation of thiosulfate is fast in neutral and acidic solutions.

For the purpose of reducing thiosulfate consumption, various researchers propose addition of sulfites and sulfates that would transform the free sulfide ion into thiosulfate during the recovery process or would retard the decomposition process by increasing the concentration of decomposition products.

Ammonium sulfate was used in the subsequent experiments as activator of the process of thiosulfate recovery of silver from the zinc cake and as inhibitor of the thiosulfate ion decomposition, in analogy to [5].

The following conclusions can be drawn from the experiments performed to determine the factors influencing the rate of recovery, the results of which are presented in Figures 1-5:

- With the increase of sodium thiosulfate concentration up to 25 g/l the rate of silver leached increases. The increase of thiosulfate concentration above 25 g/l does not result in a higher rate of silver recovery (Figure 1).
- The joint action of sodium thiosulfate and ammonium sulfate increases the rate of silver recovery. As illustrated by Figure 2, an increase of the $\text{Na}_2\text{S}_2\text{O}_3:(\text{NH}_4)_2\text{SO}_4$ ratio above 1 does not lead to further increase of the rate of silver recovery. For this reason the experiments were carried out at a ratio $\text{Na}_2\text{S}_2\text{O}_3:(\text{NH}_4)_2\text{SO}_4=1$.
- The decomposition rate of the thiosulfate leachant is directly proportional to sodium thiosulfate concentration in the solution. Upon rising of the temperature to 40 - 80°C, the thiosulfate decomposition increases four times. There are two temperature zones of thiosulfate decomposition, from 40 to 60°C and from 60 to 80°C, which are related to different decomposition mechanisms. The maximum

rate of decomposition of the thiosulfate ions is observed at 80°C and sodium thiosulfate concentration 80g/l. The experiments carried out in the temperature range up to 50°C showed that the increase of temperature above 30°C does not result in any significant increase of silver recovery from the zinc cake (Figure 3).

- The lowest rate of silver recovery is achieved at solid:liquid ratio = 1:3 (Figure 4). This is most probably due to the depletion of thiosulfate, because other metals also simultaneously pass into the solution with the silver.
- The results of the experiments showed (Figure 5) that pH of the solution does not influence the rate of silver recovery.
- In all experiments, the highest reached silver recovery degree is 74 %.

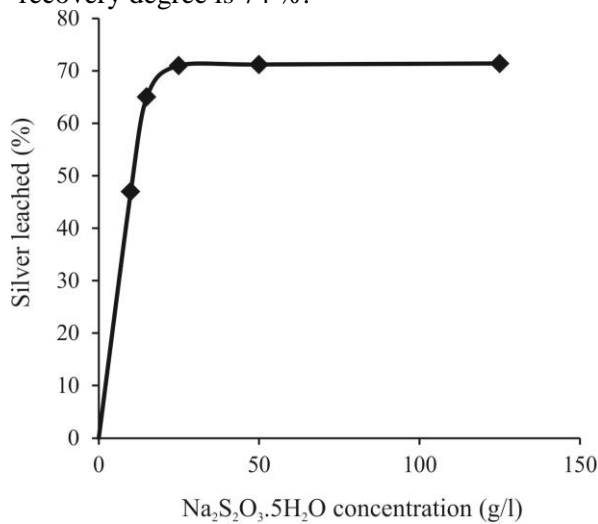


Fig. 1. Effect of thiosulfate concentration on silver leaching (T=50°C, τ=60 min, S:L=1:10, pH=6).

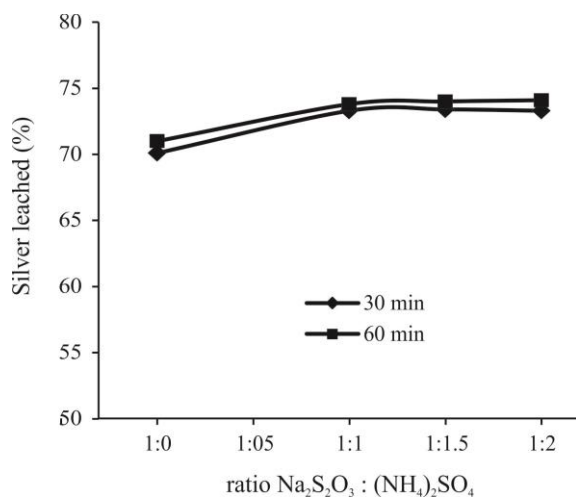


Fig. 2. Effect of ratio Na₂S₂O₃:(NH₄)₂SO₄ on silver leaching (25 g/l Na₂S₂O₃·5H₂O, T=50°C, S:L=1:10, pH=6).

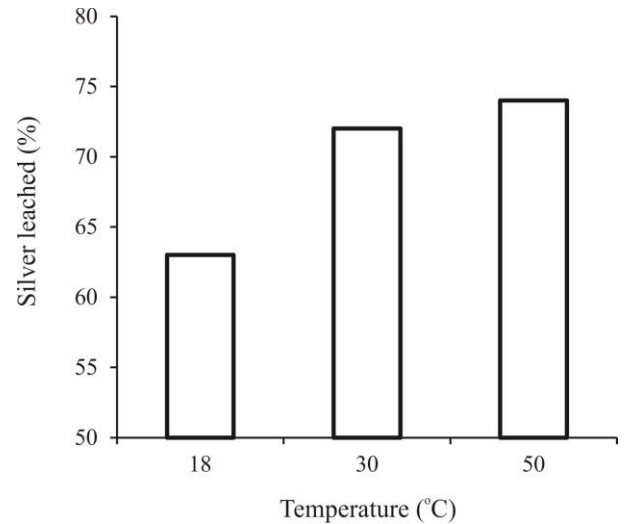


Fig. 3. Effect of temperature on silver leaching (25 g/l Na₂S₂O₃·5H₂O, 15 g/l (NH₄)₂SO₄, t=60 min, S:L=1:10, pH=6)

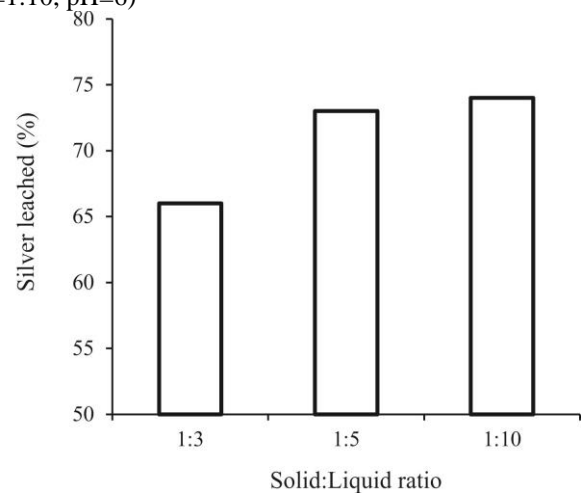


Fig. 4. Effect of solid:liquid ratio on silver leaching (25 g/l Na₂S₂O₃·5H₂O, 15 g/l (NH₄)₂SO₄, T=50°C, τ=60 min, pH=6)

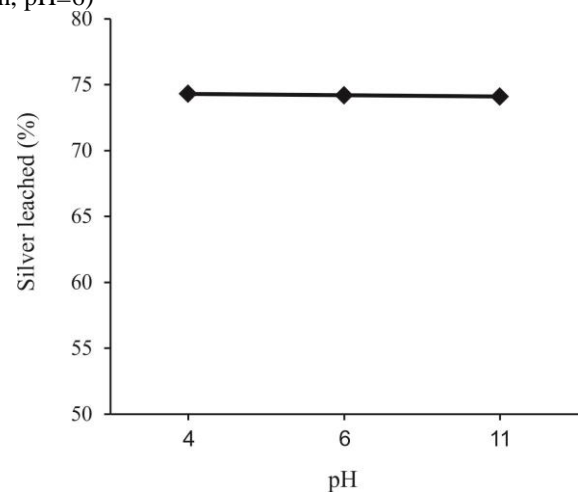


Fig. 5. Effect of pH on silver leaching (25 g/l Na₂S₂O₃·5H₂O, 15 g/l (NH₄)₂SO₄, T=50°C, S:L=1:5, τ=60 min)

As a result of thiosulfate leaching of the zinc cake at 25 g/l Na₂S₂O₃·5H₂O, 15 g/l (NH₄)₂SO₄, 20 % pulp density, 30 min process duration and pH=6, a solution with chemical composition as presented in Table 2 is obtained.

Table 1. Chemical composition of zinc cake, %

Cu	Pb	Fe	Zn	Ag, g/t
1.27	4.40	27.69	18.10	158

Table 2. Chemical composition of thiosulfate solutions, g/l

Cu	Pb	Fe	Zn	Ag
0.07	0.64	1.81	4.65	0.026

Table 3. Chemical composition of undissolved residue, %

Cu	Pb	Fe	Zn	Ag, g/t
1.14	4.85	31.95	17.00	30

As can be seen in Table 2, the thiosulfate solution contains predominantly zinc.

The chemical composition of the solid residue obtained after thiosulfate leaching of the zinc cake at these conditions is presented in Table 3.

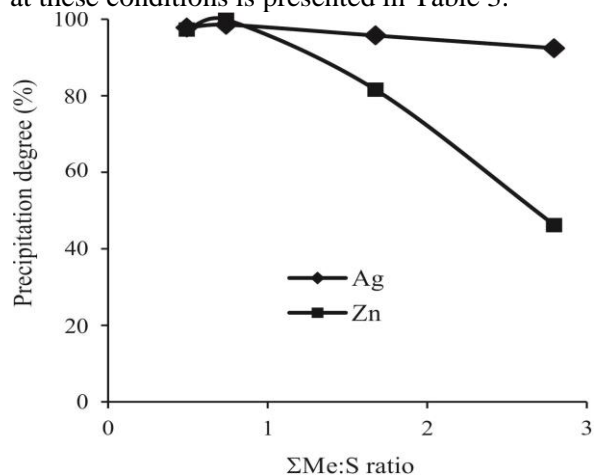
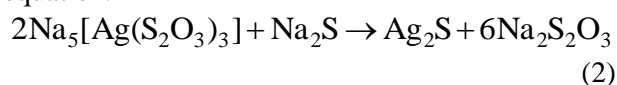


Fig. 6. Effect of ΣMe:S on precipitation degree.

Silver can be extracted from the thiosulfate solutions through cementation, electrolysis or precipitation of low-soluble compounds. The choice of a proper method will be determined by the regeneration capability of the solution. Probably the most suitable method of silver recovery is precipitation of silver sulfide by means of sodium sulfide.

3.2. Precipitation of silver from thiosulfate solutions

Of all reagents proposed for silver precipitation, sodium sulfide is the most affordable, inexpensive and reliable in terms of completeness and rate of the reaction which is described with the following equation:



Various quantities of 10 % Na₂S solution are used for metal precipitation from solution produced as a result of thiosulfate leaching of zinc cake. The dependency of the rate of silver and zinc precipitation on the ratio of the sum of metals (ΣMe) in the solution to the amount of sulphur introduced with Na₂S is presented in Figure 6.

Depending on the quantity of Na₂S, pH of the thiosulfate solution varies from 6 to 11, whereupon, to different degrees, the zinc is precipitated as a hydroxide. The chemical composition of the hydroxide-sulfide precipitate obtained at ΣMe:S = 0,74 is presented in Table 4.

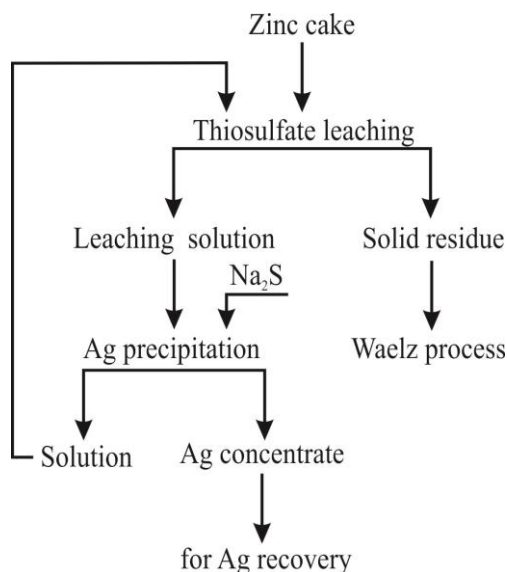


Fig. 7. Conceptual flow sheet for treatment of zinc cake.

Table 4. Chemical composition of sulfide concentrate, %

Cu	Pb	Fe	Zn	Ag	S
0.93	3.55	0.27	43.09	0.1616	10.74

Table 5. Metal precipitation degree, %

Cu	Pb	Fe	Zn	Ag
97.80	99.58	92.32	99.93	99.99

Table 6. Chemical composition of leaching solution (pH=7) and obtained concentrate

	Cu	Pb	Fe	Zn	Ag
Leaching solution, g/l	0.334	0.122	0.016	6.5	0.115
Concentrate, %	14.29	5.65	0.19	44.73	5.18

In that case, the degree of precipitation of the examined metals varies between 92 and 100% (Table 5). The technology of thiosulfate recovery of silver from zinc cake is attractive only if the solution is regenerated and reused, in which case the silver concentration is gradually increased to higher levels. Experiments for repeated use of the thiosulfate solution for dissolution of new batches of zinc cake were carried out and the precipitator consumption is being determined by the ratio $\Sigma\text{Me}:\text{S} = 1$. It was found that upon dissolution of the second batch of cake the degree of silver recovery decreased from 74 % to 6 %, which was due to the presence of free S^{2-} , because of the high consumption of precipitator. Therefore, for successful regeneration of the thiosulfate solution the leaching process should be performed while maintaining pH=7-8, so as to secure hydrolyzation of the other metals except silver. Then, the consumption of precipitator will be considerably lower. For that purpose, experiments were carried out for quintuple use of the thiosulfate solution while maintaining pH=7 by means of lime milk. The consumption of sodium sulfide for silver precipitation is 1,1 g per 1 g of silver in the solution. After recovery of the fifth batch the thiosulfate solution has the chemical composition presented in Table 6. The chemical composition of the hydroxide-sulfide concentrate obtained after precipitation is also presented in the same table.

As a result of the quintuple use of the thiosulfate solution, the rate of silver recovery in the concentrate decreases from 74 to 70 %. It means that the thiosulfate solution should be adjusted at regular intervals. It can be assumed that if an even higher pH is maintained during the recovery, for example pH=8, whereby fuller hydrolyzation of the

metals is secured, the silver content in the produced concentrate will increase significantly.

For treatment of the solid residue after thiosulfate leaching there are two possible ways – Waelz-process or floatation and Waelz-process.

The conceptual flow sheet for treatment of the zinc cake is presented in Fig. 7.

CONCLUSIONS

As demonstrated by the obtained experimental results, about 74% of the silver contained in the zinc cake can be recovered by thiosulfate technology and subsequent precipitation with Na_2S to produce silver concentrate. The proposed process diagram can be successfully applied in the end of the cycle of wet recovery of zinc cakes.

REFERENCES

1. N. B. Kokoeva, *Trudy molodykh uchenykh*, **2**, 35 (2005).
2. M.G Aylmore, D.M Muir, *Minerals Engineering*, **14**, 135 (2001).
3. J. L. Deutsch and D. B. Dreisinger, *Hydrometallurgy*, **137**, 156 (2013).
4. J. L. Deutsch, D. B. Dreisinger, *Hydrometallurgy*, **137**, 165 (2013).
5. Maksimov, O. K. Kuznetsov, N. V. Khodov, V. M. Alkatsev, N. I. Bekarevich, I. S. Sataev, L. A. Otrozhdennova, N. D. Malinovskaya, *RU Patent* 2002828 (1993).
6. L. A. Otrozhdennova, N. D. Malinovskaya, I. I. Maksimov, N. D. Khodov, O. K. Kuznetsov, *XIX IMPC Precious Metals Processing & Mineral Waste & the Environment*, San Francisco Vol. 4, (1995), pp. 75-77.
7. V. V. Geykhan, L. A. Kazanbaev, P. A. Kozlov, A.V.Kolesnikov, V. B. Chinkin, *Tsvetnye Metally (Non-Ferrous Metals)*, **1**, 25 (2003).

ИЗВЛИЧАНЕ НА СРЕБРО ОТ ЦИНКОВИ КЕКОВЕ

Б. И. Лучева *, П. К. Илиев, Вл. П. Стефанова

Департамент по цветни метали, Химико-технологичен и металургичен университет, София 1718, България

Постъпила на 27 юни, 2014 г.; приета на 8 април, 2014 г.

(Резюме)

В настоящата експериментална работа е изследвана възможността за тиосулфатно извличане на среброто от цинковите кекове, получени при мокрото извличане на цинкова угарка в КЦМ-Пловдив. Изследвано е влиянието на различни фактори върху степента на тиосулфатно извличане на среброто. Установено, че степента на извличане на среброто е 70-74 % в температурния диапазон 30-50°C при плътност на пулпа 20% и времетраене на извличането 30 min, независимо от рН на разтвора. Проследено е поведението на медта, оловото, цинка и желязото при тиосулфатното извличане. При поддържане на рН на тиосулфатния разтвор 7-8 с цел хидролизиране на металите, преминали в разтвора и следващо утаяване на среброто с Na_2S се получава сребърен концентрат. Разгледана е възможността за регенериране на тиосулфатния разтвор. Твърдият остатък от извличането съдържа 10-40 g/t и може да бъде преработван чрез Велц-процес.

Application of waste glycerol from biodiesel production for obtaining of modifiers for reduced friction of different motor oils

Z. Glavcheva-Laleva¹, L. Varadinova², St. Kerekov³, D. Pavlov⁴, Iv. Glavchev^{2*}

¹Institute for Organic Chemistry, Bulgarian Academy of Science, Acad. G. Bonchev Street, Building 9, 1113 Sofia, Bulgaria, ²University of Chemical Technology and Metallurgy, Sofia, Bulgaria, ³Director "NITIA" OOD, Sofia, Bulgaria, ⁴University of Russe „Angel Kanchev”, Russe, Bulgaria

Received August 11, 2014; Revised April 8, 2015

Glycerol mono oleate (GMO) was made from waste glycerol (WG) from biodiesel productions by condensation with oleic acid in presence of titanium alcoholate as catalyst. The total acid number was obtained with titration of the samples of GMO with alcohol solution of potassium hydroxide (ASKON). The neutralization of extra oleic acid was made by alcohol solution of methyl amine or 25% ammonia. The prepared sample from the obtained modifier was analysed by standard method with four-ball method and the reduced friction was assessed.

Key words: waste glycerol, glycerol monooleate, titanium catalysts, friction modifiers

INTRODUCTION

In a number of publications was described the obtaining of GMO started from 30th years of the last century. It was known that this compound can be obtain from:

- Glycerolize
- Hydrolyses of triglycerides
- Direct esterification of glycerol with oleic acid

The third method was possible to be made with or without catalysts. The first possibility was made usually at high temperature or pressure. The applied catalysts were acids [1,2] or basis [3,4]. Usually the application of catalysts decreases the temperature and the time. The application of solid catalysts (oxides, zeolites and others) widely investigated and it will not be described in this paper. The reaction between oleic acid (OA) and ammonia or amines was well known, because $-\text{COOH}$ was acidic, but amines were bases. In [6] was described the obtaining of amides from fatty acids and methylamine. The same authors have another article, published in 2013 year. The application of enzymes was described in a lot of articles [7]. We investigated the possibility for making of glycerol mono oleate from waste glycerol obtained in biodiesel production. The reaction was made in the presence of a new titan tetra alcoholic containing catalysts (TiAl) applied in syntheses of synthetic oils [8]. Because they have some excess of oleic acid, we decided to combine it with methyl

amine. The reaction between glycerol $-\text{OH}$ groups and oleic acid in the presence of TiAl was investigated at two temperatures and the activation energy ($E_{\text{act.}}$) was determined.

EXPERIMENTAL

The compound WG was investigated by elemental analysis (EA) with apparatus Euro EA 3000 (Euro Vector Sp A, Italy). The carbon, nitrogen and hydrogen content were measured in the analyzed samples by burning of the material with weight 0.5 – 1.5 mg at 980°C in oxygen atmosphere. The obtained gas mixture passed through chemical/absorption zone. Then CO_2 , N_2 and H_2O were separated by gas chromatography. It was known, that glycerol have no nitrogen in his molecule, but in WG it was possible to have some small amount of nitrogen from protein of the raw oils applied in biodiesel production. The standard curve was made through analyses of acetone (C₃H₆O) with computer product Calligus. From the obtained results, the content of glycerol (G) was calculated. The results from EA were compared by data obtained with UV-VIS analyses, made by apparatus Cary 100 Scan UV-VIS spectrophotometer (Varian, Germany) by obtaining the spectra of WG and pharmacopeius G, 99% product of Chemapol Ltd, Dimitrograd, Bulgaria and of G, p.a., product of Valerus Ltd, Sofia, Bulgaria. From the obtained spectra of the second company, the dependence concentration of G – C, / absorption A was made and there were calculated the equations of several maxima in the specter of G with different values of accuracy of the obtained

* To whom correspondence should be sent.
E-mail: ivgl@uctm.edu

equations and experimental values (correlation coefficient R^2). With the equations at 222 nm and A from spectrum of WG it was calculated the glycerol content in the WG. The obtained value was 62%. The syntheses of GMO were made in 150°C for 3 h in the presence of 0.43 ml TiAl, 0.5 mol. standard OK, p.a., product of Valerus Ltd. and 0.6 mol. WG. The same synthesis was made with standard OK and G, p.a. The obtained products were investigated by ^1H NMR (by apparatus Bruker Avance DRX250), UV-VIS and FTIR spectroscopies (by apparatus Cary 100 Scan UV-VIS and Varian FTIR). The investigation with UV-VIS were made in 10 mm cuvettes. The investigation with FTIR were made in thin layers of the obtained materials. The friction properties of GMO obtained from WG and from pure raw materials were investigated by standard method like additive of engine oil with four ball machine [9].

RESULTS AND DISCUSSION

The characteristics of WG were investigated with elemental analyses, UV-VIS and FTIR spectroscopies. The spectra of G, product of Chemapol Ltd, Dimitrovgrad, Bulgaria were made with UV-VIS spectroscopy but they have not maxima in the area 200 – 400 nm (fig. 1).

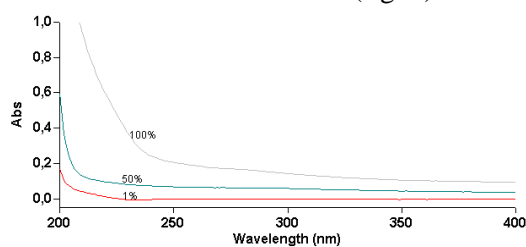


Fig. 1. UV-VIS spectra of G, product of Chemapol Ltd, Dimitrovgrad

The spectra of glycerol published in the literature have several maxima in this area. This is the reason to make the same investigations with G, p.a., product of Valerus Ltd, Sofia, Bulgaria. The obtained spectra are presented in fig.2

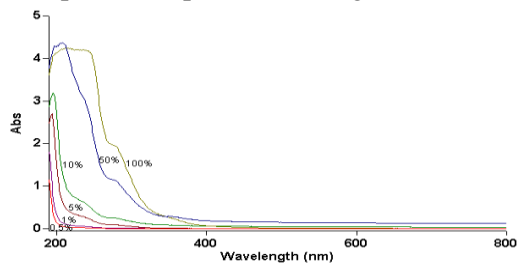


Fig. 2. UV-VIS spectra of G, product of Valerus Ltd, Sofia, Bulgaria

From the obtained spectra were made equations concentration C, % / absorption A for maxima at

285, 225, 222 and 218 nm. It was known, that the equations are true if $R^2 > 0.99$. This is the reason to make calculations only with equation at 222 nm. From this equation and from the data for WG given in fig. 3 the concentration of G in WG was calculated, namely 62%.

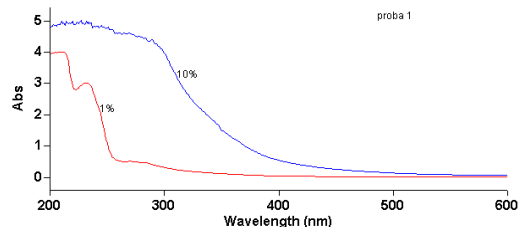


Fig. 3. UV-VIS spectra of water solutions of WG

In ^1H NMR spectrum of WG have maxima for protons in $-\text{CH}-$, $-\text{CH}$ и $-\text{OH}$ groups. These groups were with bands, shown in FTIR spectrum of WG. For example $-\text{OH}$ was with band at 3354.45 cm^{-1} . Because WG was very reactive, was made spectrum in thin layer on the plate from CaF_2 with apparatus ThermoScientific Nicolet 6700

GMO, obtained from WG and standard OA, like product, made only from standard G and OA were investigated with ^1H NMR, UV-VIS and FTIR spectroscopies. Data for ^1H NMR of GMO, made from WG was analogical of data for this compound, published in [10]. In fig. 4 was given UV-VIS spectrum of GMO from WG and standard OA. The place of two maxima for 1% -en alcohol solution of GMO was under of 300 nm

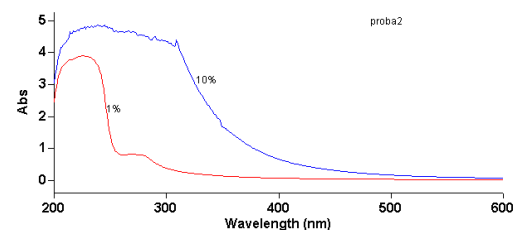


Fig. 4. UV-VIS spectra of alcohol solutions of GMO, made from WG with TiA.

FTIR spectrum of GMO, obtained with the same catalyst from WG and standard OA was shown in fig. 5. The bands for $-\text{OH}$ group was at 3382.660 cm^{-1} , for $-\text{CH}-$ and CH_2 groups were at 2926.058 , 2853.929 , 1463.020 , 1410.009 and 723.009 cm^{-1} and for $-\text{CO}$ was at 1711.729 cm^{-1} . The values of some bands were at the same position, like in row glycerol, but in some bands were in a new places, because were for a new compound. In FTIR spectrum of GMO, obtained at the same catalyst from standard raw materials, shown in fig. 7 had the same bands. The differences in the values of some bands were so small, that were after decimal point.

In the spectra of GMO after neutralization of the remained acids with alcohol solution of methylamine ore with 25% water solution of ammonia, shown in figures 7 and 8 had analogical bands.

The activation energy E_{act} of the esterification of $-OH$ groups in GMO with OA was obtained in the investigation of the reaction in two temperatures –

room at $80^{\circ}C$. From the values of the velocities $W_1 = 0.052$ mg KOH/g.h. and $W_2 = 0.7515$ mg.

KOH/g.h. was obtained the value of activation energy $E_{act} = 9.15$ kJ/mol. The values of acid numbers (AN) were obtained with alcohol solution of KOH by standard method, described in [11]. The obtained values were in table 1.

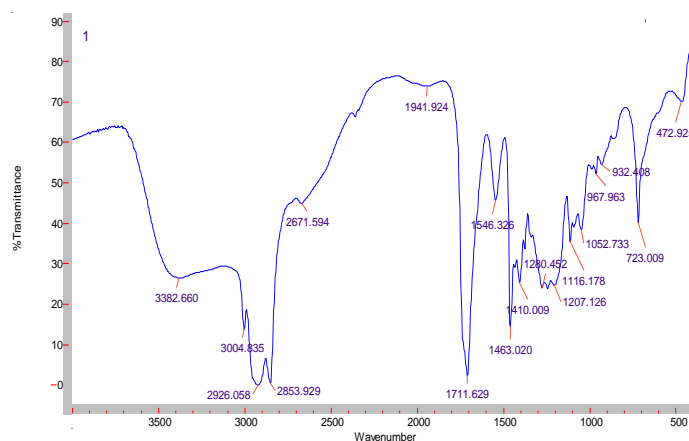


Fig 5 FTIR spectrum of GMO, obtained from WG and standard OA with TiAl

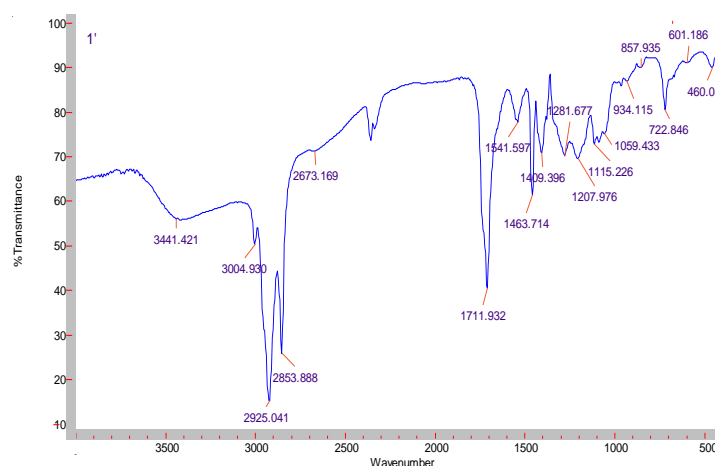


Fig. 6. FTIR spectrum of GMO, obtained from standards G and OA with TiAl.

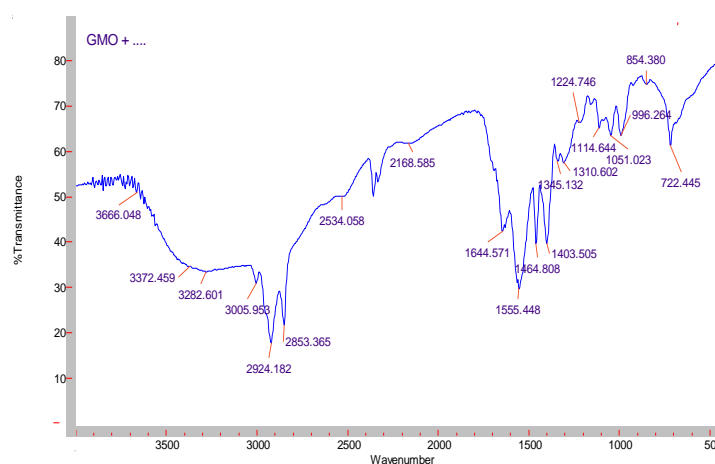


Fig. 7. FTIR spectrum of GMO, obtained from WG with catalyst TiAl and after neutralization of the remained acids with alcohol solution of methylamine.

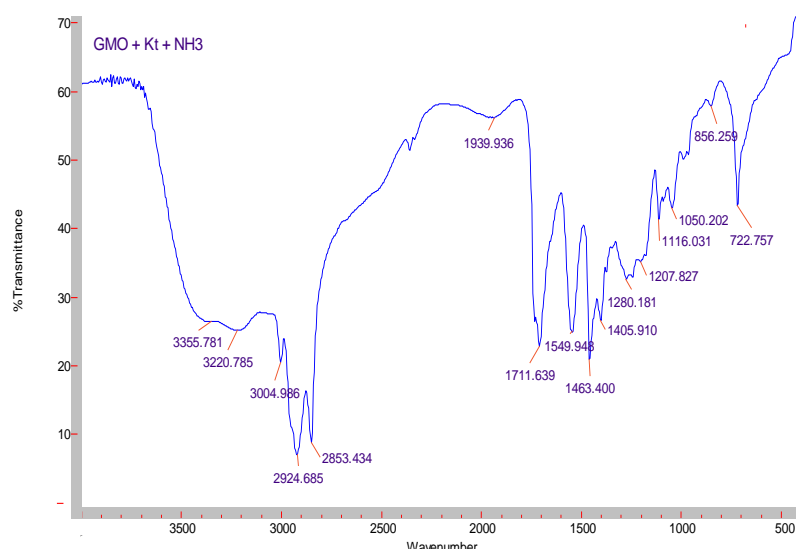


Fig. 8. FTIR spectrum of GMO obtained from WG with catalyst TiAl and after neutralization of the remained acids with water solution of 25% ammonia

Table 1. Data for A.N. of GMO and its mixtures with methylamine (MA)(1 -11.02, 2 – 19.02, 3 – 02.04)in room temperature

N	Probe (ml/ml)	A.N.1,mg KOH*/ g	A.N. 2,mg KOH*/ g	A.N..3,mg KOH*/ g
1	GMO from WG	101.15	80.53	79.68
2	GMO: MA= 5 : 1	71.34	51.78	51.55
3	GMO: MA = 5 : 3	61.97	alkaline	alkaline
4	GMO: MA = 5 : 5	42.28	alkaline	alkaline

Table 2. Dependences between average diameter of wearing of the balls (d_{eva}) and of anti wearing index (AWI),from the quantity, % and the kind of investigated modifiersin mineral motor oil M10D₂/E₁

№	Quantity,% and the kind of modifier ,	d_{eva} of wearing,mm	AWI, N
1	0	0.60	243
2	2, Zn succinide	0.36	346
3	0.5, Zn succinide	0.39	329
4	0.5, Cu oleate	0.45	-
5	GMO obtained from WG	0.43	302
6	GMO obtained from standard materials	0.42	324

Table3. Dependences between average diameter of wearing of the balls (d_{av}), %, Δ from the quantity, % and the kind of investigated modifiersin motor oilSN 500

№	Quantity,% and the kind of modifier ,	d_{av} of wearing, mm., %, Δ
1	0 , Mineral motor oil SN 500,	0.70, 100, 0
2	1, anilidoleate	0.57, 81.43, 18.57
3	0.5, anilidoleate	0.62, 88.57, 11,43
4	1, Cu oleate	0.65, 92.86, 7.14
5	0.5, Cu oleate	0.60, 85.71, 14.29
6	2, Complex polyester	0.63, 90, 10
7	1, Complex polyester	0.63, 90, 10
8	2, GO obtained from WG	0.60, 85,71, 14.29
9	1, GO obtained from WG	0,56, 80, 20
10	0,5, GO obtained from WG	0,56, 80, 20
11	2, GO obtained from standard materials	0.60, 85.71, 14.29
12	1, GO obtained from standard materials	0,55, 78.57, 21.13
13	0,5, GO obtained from standard materials	0,55, 78.57, 21.13

Table 4. Dependences between average diameter of wearing of the balls (d_{av}), %, Δ from the quantity, % and the kind of investigated modifiersin synthetic motor oil5W40 according SAESL/CF по API

№	Quantity,% and the kind of modifier ,	d _{av} of wearing, mm., %, Δ
1	0 , syntetic motor oil 5W40	0.59, 100, 0
2	1, anilidoleate	0.53, 89.83, 10.17
3	0.5, anilidoleate	0.54, 91.53, 8.47
4	1, Cu oleate	0.50, 84.75, 15.24
5	0.5, Cu oleate	0.55, 93.22, 6.78
6	2, Complex polyester	0.47, 79.66, 20.34
7	1, Complex polyester	0.50, 84.75, 15.24
8	0,5, Complex polyester	0.55, 93.22, 6.78
8	2, GO obtained from WG	0.55, 93.22, 6.78
9	1, GO obtained from WG	0.55, 93.22, 6.78
10	0,5, GO obtained from WG	0.54, 91.53, 8.47
11	2, GO obtained from standard materials	0.52, 88.14, 11.86
12	1, GO obtained from standard materials	0.52, 88.14, 11.86
13	0,5, GO obtained from standard materials	0.54, 91.53, 8.47
14	1, Zn oleate	0.55, 93.22, 6.78
15	0,5, Zn oleate	0.55, 93.22, 6.78
16	1, Titanium oleate	0.52, 88.14, 11.86
17	0,5, Titanium oleate	0.55, 93.22, 6.78

Data for AN of GMO, obtained at 80°C were analogical. MA was 33% solution of the gaze CH₃NH₂ in pure ethanol. If the sample was alkaline was not possible the determination of AN. Maybe the esterification of GMO and OA prolonged, because in the molecule of Ghave 3 OH groups, capable to react with – COOH groups of OA. In the presence of MA this possibility increased (probes NN 3 and 4).

The properties of the obtained compounds like friction modifier of different motor oils were determined with four ball machine by standard method. For comparison were made investigations with standard friction modifiers. The investigations were made in acidities laboratory for oil products of "Prista Oil" Ltd. In 120°C for 1h – table 2 and in laboratories of university of Russe "Angel Kanchev", given in tables 3, and 4.

From the results, shown in table 2 was evident, that anti wearing properties of the oil with frictions modifiers (d_{eva} mm and AWI) increased with friction modifier Zn succinidewith 30%. With the decreasing of the concentration of the modifier those % was decreased from d_{eva}= 0,36mm for 2% to 0,39 mm for 0,5%, but was enough for anti wearing properties of motor oil. With anti wearing modifier Cu oleate were obtained the best results, compared with results of friction modifier GMO, obtained with catalyst TiAl. From the data in table 2 was evident, that the modifier GMO, made from WG and OA were similar with the anti wearing properties of GMO, obtained from standard materials. The increasing was about 25%. From the results, shown in tables 3 and 4 were evident, that the obtaining materials were the good frictions modifiers

CONCLUSION

The results for decreasing of the quantity of different friction modifiers, given in tables 2, 3 and 4 in mineral and synthetic motor oils were not every time in connection with theory of friction modifiers, but the results, obtained with investigated materials from WG were comparable or better with data, obtained with known friction modifiers.

Acknowledgment: This study is a part of our investigations and fulfilling of the scientific project "Modifiers for reducing the friction and wear in machinery", financed by Operational programme "Development of the Competitiveness of the Bulgarian Economy" 2007-2013.

We thanks to Assoc. Prof. Galina Gencheva, PhD, Laboratory of Molecular Spectroscopy, Department of Analytical Chemistry, faculty of Chemistry and Pharmacy, Sofia University for permit ion of making of FTIR spectrum of WG.

REFERENCES

1. Is. Díaz, C. Márquez-Alvarez, F. Mohino, J. P. Pariente¹, E. Sastre, *Journal of Catalysis*, **193-2**, 295 (2000).
2. Is. Díaz, F. Mohino, J. Pérez-Pariente, E. Sastre, *Applied Catalysis A: General*, **242-1**, 161 (2003).
3. M. Berrios, J. Siles, M. A. Martín, A. Martín, *Fuel*, **86-15**, 2383 (2007).
4. M. Zong, Z. QunDuan, W. Lou, T. J. Smithand, H. Wu, *Green Chemistry*, **5**, (2007).
5. S. Abro, Y. Pouilloux, J. Barroult, *Stud. Surf. Sci. Catal*, **108**, 539 (1997).

6. F. Ergan, M. Trani, G. André, *Biotechnology and Bioengineering*, **35**, 195 (1990).
7. O. Abel-Anyebe, K. I. Ekpenyong, A. Eseyin, *International Journal of Chemistry*, **5-1**, 80 (2013).
8. D. J. Pavlov, N. N. Gospodinova, I. K. Glavchev, *Industrial Lubrication and Tribology*, **56**, 19 (2004).
9. BSS 9786-84
10. C. Yu, Y. Lee, B. Cheon, S. Lee, *Bull. Korean Chem. Soc.*, **24** 1224 (2003).
11. БДС EN ISO 660 – 2009.

ПРИЛОЖЕНИЕ НА ОТПАДЪЧЕН ГЛИЦЕРОЛ ОТ ПРОИЗВОДСТВОТО НА БИОДИЗЕЛ ЗА ПОЛУЧАВАНЕ НА МОДИФИКАТОР НА ТРИЕНЕ НА РАЗЛИЧНИ МОТОРНИ МАСЛА

З. Главчева-Лалева¹, Л. Варадинова², Ст. Кереков³, Д. Павлов⁴, Ив. Главчев²

¹Институт по Органична химия, Българска академия на науката, Акад. „Г.Бончев”, сгр. 9, 1113 София, България,

²Университет по химична технология и металургия, София, България,

³Директор „НИТИАТ” ООД, София, България,

⁴Университет на Русе, „А.Кънчев”, Русе, България

Постъпила на 11 август, 2014 г., коригирана на 8 април, 2015 г.

(Резюме)

Глицерол моно олеат (ГМО) беше получен от отпадъчен глицерол (ОГ) от производството на биодизел при кондензация с олеинова киселина с катализатор титанов алкохолат. Общото киселинно число беше получено с титруване на проби от ГМО с алкохолен разтвор на калиева основа (АРКОН). Неутрализацията на излишната олеинова киселина беше направено с алкохолен разтвор на метиламин или 25% амоняк при стайна температура. Получените проби от модификатора на триене бяха изследвани със стандартен метод с четирисачмяна машина и промяната на триенето беше оценена.

BULGARIAN CHEMICAL COMMUNICATIONS

Instructions about Preparation of Manuscripts

General remarks: Manuscripts are submitted in English by e-mail or by mail (in duplicate). The text must be typed double-spaced, on A4 format paper using Times New Roman font size 12, normal character spacing. The manuscript should not exceed 15 pages (about 3500 words), including photographs, tables, drawings, formulae, etc. Authors are requested to use margins of 3 cm on all sides. For mail submission hard copies, made by a clearly legible duplication process, are requested. Manuscripts should be subdivided into labelled sections, e.g. **Introduction, Experimental, Results and Discussion, etc.**

The title page comprises headline, author's names and affiliations, abstract and key words.

Attention is drawn to the following:

a) **The title** of the manuscript should reflect concisely the purpose and findings of the work. Abbreviations, symbols, chemical formulas, references and footnotes should be avoided. If indispensable, abbreviations and formulas should be given in parentheses immediately after the respective full form.

b) **The author's** first and middle name initials, and family name in full should be given, followed by the address (or addresses) of the contributing laboratory (laboratories). **The affiliation** of the author(s) should be listed in detail (no abbreviations!). The author to whom correspondence and/or inquiries should be sent should be indicated by asterisk (*).

The abstract should be self-explanatory and intelligible without any references to the text and containing not more than 250 words. It should be followed by key words (not more than six).

References should be numbered sequentially in the order, in which they are cited in the text. The numbers in the text should be enclosed in brackets [2], [5, 6], [9–12], etc., set on the text line. References, typed with double spacing, are to be listed in numerical order on a separate sheet. All references are to be given in Latin letters. The names of the authors are given without inversion. Titles of journals must be abbreviated according to Chemical Abstracts and given in italics, the volume is typed in bold, the initial page is given and the

year in parentheses. Attention is drawn to the following conventions:

a) The names of all authors of a certain publications should be given. The use of “*et al.*” in the list of references is not acceptable.

b) Only the initials of the first and middle names should be given.

In the manuscripts, the reference to author(s) of cited works should be made without giving initials, e.g. “Bush and Smith [7] pioneered...”. If the reference carries the names of three or more authors it should be quoted as “Bush *et al.* [7]”, if Bush is the first author, or as “Bush and co-workers [7]”, if Bush is the senior author.

Footnotes should be reduced to a minimum. Each footnote should be typed double-spaced at the bottom of the page, on which its subject is first mentioned.

Tables are numbered with Arabic numerals on the left-hand top. Each table should be referred to in the text. Column headings should be as short as possible but they must define units unambiguously. The units are to be separated from the preceding symbols by a comma or brackets.

Note: The following format should be used when figures, equations, *etc.* are referred to the text (followed by the respective numbers): Fig., Eqns., Table, Scheme.

Schemes and figures. Each manuscript (hard copy) should contain or be accompanied by the respective illustrative material as well as by the respective figure captions in a separate file (sheet). As far as presentation of units is concerned, SI units are to be used. However, some non-SI units are also acceptable, such as °C, ml, l, etc.

The author(s) name(s), the title of the manuscript, the number of drawings, photographs, diagrams, etc., should be written in black pencil on the back of the illustrative material (hard copies) in accordance with the list enclosed. Avoid using more than 6 (12 for reviews, respectively) figures in the manuscript. Since most of the illustrative materials are to be presented as 8-cm wide pictures, attention should be paid that all axis titles, numerals, legend(s) and texts are legible.

The authors are asked to submit **the final text** (after the manuscript has been accepted for

publication) in electronic form either by e-mail or mail on a 3.5" diskette (CD) using a PC Word-processor. The main text, list of references, tables and figure captions should be saved in separate files (as *.rtf or *.doc) with clearly identifiable file names. It is essential that the name and version of the word-processing program and the format of the text files is clearly indicated. It is recommended that the pictures are presented in *.tif, *.jpg, *.cdr or *.bmp format, the equations are written using "Equation Editor" and chemical reaction schemes

are written using ISIS Draw or ChemDraw programme.

The authors are required to submit the final text with a list of three individuals and their e-mail addresses that can be considered by the Editors as potential reviewers. Please, note that the reviewers should be outside the authors' own institution or organization. The Editorial Board of the journal is not obliged to accept these proposals.

EXAMPLES FOR PRESENTATION OF REFERENCES

REFERENCES

1. D. S. Newsome, *Catal. Rev.–Sci. Eng.*, **21**, 275 (1980).
2. C.-H. Lin, C.-Y. Hsu, *J. Chem. Soc. Chem. Commun.*, 1479 (1992).
3. R. G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford Univ. Press, New York, 1989.
4. V. Ponec, G. C. Bond, *Catalysis by Metals and Alloys* (Stud. Surf. Sci. Catal., vol. 95), Elsevier, Amsterdam, 1995.
5. G. Kadinov, S. Todorova, A. Palazov, in: *New Frontiers in Catalysis* (Proc. 10th Int. Congr. Catal., Budapest, 1992), L. Guzzi, F. Solymosi, P. Tetenyi (eds.), Akademiai Kiado, Budapest, 1993, Part C, p. 2817.
6. G. L. C. Maire, F. Garin, in: *Catalysis. Science and Technology*, J. R. Anderson, M. Boudart (eds), vol. 6, Springer-Verlag, Berlin, 1984, p. 161.
7. D. Pocknell, *GB Patent 2 207 355* (1949).
8. G. Angelov, PhD Thesis, UCTM, Sofia, 2001.
9. JCPDS International Center for Diffraction Data, Power Diffraction File, Swarthmore, PA, 1991.
10. *CA* **127**, 184 762q (1998).
11. P. Hou, H. Wise, *J. Catal.*, in press.
12. M. Sinev, private communication.
13. <http://www.chemweb.com/alchem/articles/1051611477211.html>.

CONTENTS

<i>N. Yavorov, St. Petrin, I. Valchev, S. Nenkova</i> , Potential of fast growing poplar, willow and palownia for bioenergy production.....	5
<i>D.I. Zheleva</i> , Comparative analyses of keratin biocomposites with composites based on collagen.....	10
<i>Ts.N. Ilieva, S.K. Nenkova, M. Herzog</i> , Artificial ageing of composites based on modified cellulose fibres and polyurethane prepolymer.....	16
<i>R. Boeva, I. Spiridonov, R. Nikolov, G. Radeva</i> , Investigation of thermal ageing of chemical mechanical pulps obtained from different types of hardwood.....	21
<i>K.V. Dimitrov, A. Matev, M. Herzog, S. Nenkova</i> , Thermoforming – process of biopolymer composites.....	25
<i>S. Petrin, N. Yavorov, P. Tzvetkov, I. Valchev, G. Radeva</i> , Kinetic aspects of enzyme hydrolysis of cellulose fiber material.....	30
<i>S.A.Kotlarova, V.G.Lasheva, D.A.Todorova</i> , Ecological utilization of printed waste paper.....	34
<i>N. Rangelova, S. Nenkova, N. Lazarova, N. Georgieva</i> , Copper-based nanostructured lignocellulose materials with antibacterial activity.....	39
<i>D.A. Todorova, S.P. Bencheva</i> , Investigation on the influence of chemical additives over the behavior of paper furnish from recycled fiber material.....	43
<i>V. Radkova, P. Tsekova, T. Ivanova and I. Valchev</i> , Effect of dry-heat ageing on label paper quality.....	51
<i>T.Tc. Bozhkova, I.T. Spiridonov, Y.V. Nedelchev, R.K. Boeva, A.M. Ganchev</i> , Improvement of the physical-mechanical and optical properties of printing production with biodegradable overprint varnishes.....	60
<i>M.N. Kamburov, T.V. Ivanov, I.G. Lalov</i> , Immobilization of glucose oxidase on porous copolymer.....	64
<i>T.V. Ivanov, I.G. Lalov, L.K. Yotova</i> , Denitrification of wastewater with immobilized cells of <i>Pseudomonas denitrificans</i>	70
<i>P.E. Marinova, M.N. Marinov, M. H. Kazakova, Y.N. Feodorova, V.S. Sarafian, N.M Stoyanov</i> , Synthesis and bioactivity of new platinum and ruthenium complexes of 4-bromo-spiro-(fluorene-9,4'-imidazolidine)-2',5'-dithione.....	75
<i>P.P. Petrova, S.M. Miloshev, Ch.P. Novakov</i> , Cross-linked star (co)polymers containing core of C-tetraalkylcalix[4]resorcinarene.....	79
<i>N. Marinov, M. Simeonova</i> , Preparation of poly(ethylcyanoacrylate) nanofibers by vapor phase polymerization using alcohol initiators.....	87
<i>V. Staneva, G. Ivanova, M. Simeonova</i> , Surface modified poly (butyl cyanoacrylate) nanoparticles loaded with indomethacin: preparation and physicochemical characterization ..	93
<i>I.T. Spiridonov, R. K. Boeva, T. Tz. Bozhkova, Y. V. Nedelchev</i> , Investigation on the effect of different tone value sum (tac) of inks on the color reproduction accuracy of heatset web offset images.....	100
<i>P. Iliev, V. Stefanova, B. Lucheva</i> , Sulfuric acid autoclave dissolution of Ni-Co sulfide deposit.....	106
<i>B.I. Lucheva, P.K. Iliev, Vl.P. Stefanova</i> , Recovery of silver from zinc cakes.....	112
<i>Z. Glavcheva-Laleva, L. Varadinova, St. Kerekov, D. Pavlov, Iv. Glavchev</i> , Application of waste glycerol from biodiesel production for obtaining of modifiers for reduced friction of different motor oils.....	118
<i>Instructions to authors</i>	124

СЪДЪРЖАНИЕ

<i>Н. Яворов, Ст. Петрин, И. Вълчев, С. Ненкова</i> , Изследване потенциала на бързорастяща топола, върба и пауловния за получаване на биоенергия.....	9
<i>Д. И. Желева</i> , Преглед и сравнителен анализ на кератинови биокompозити с такива на база колаген.....	15
<i>Цв. Н. Илиева, С. К. Ненкова, М. Херцог</i> , Изкуствено стареене на композитни материали, получени от модифицирани целулозни влакна и полиуретанов преполимер.....	20
<i>Р. Боева, И. Спиридонов, Р. Николов, Г. Радева</i> , Изследване на термичното стареене на химико механични маси, получени от различни видове широколистна дървесина	24
<i>К. Димитров, А. Матев, М. Херцог, С. Ненкова</i> , Термоформуване на био-базирани композити.....	29
<i>С. Петрин, Н. Яворов, П. Цветков, И. Вълчев, Г. Радева</i> , Кинетични аспекти на ензимната хидролиза на целулозен влакнест материал.....	33
<i>С. Котларова, В. Лашева, Д. Тодорова</i> , Екологично оползотворяване на отпадъчна хартия с печат.....	41
<i>Н. Рангелова, С. Ненкова, Н. Лазарова, Н. Георгиева</i> , Медни нано-структурирани лигноцелулозни материали с антибактериално действие.....	44
<i>Д. А. Тодорова, С. П. Бенчева</i> , Изследване влиянието на химически спомагателни вещества върху поведението на суспензия от рециклиран влакнест материал от вестници	50
<i>В. Радкова, П. Цекова, Т. Иванова, И. Вълчев</i> , Влияние на термичното стареене върху качествата на хартия за етикети.....	59
<i>Т. Божкова, И. Спиридонов, Я. Неделчев, Р. Боева, А. Ганчев</i> , Подобряване на физико-механичните и оптични характеристики на печатната продукция с биоразградим надпечатан лак.....	63
<i>М. Н. Камбуров, Т. В. Иванов, И. Г. Лалов</i> , Имобилизирание на глюкозооксидаза в порьозен съполимер.....	69
<i>Т.В. Иванов, И.Г. Лалов, Л.К. Йотова</i> , Денитрификация на отпадни води с имобилизирана биомаса от <i>Pseudomonas denitrificans</i>	73
<i>П. Е. Маринова, М. Н. Маринов, М. Х. Казакова, Я. Н. Феодорова, В. С. Сарафян, Н. М. Стоянов</i> , Синтез и биологична активност на нови Pt(II) и Ru(III) комплекси на 4-бromo-спиро-(флуорен-9,4'-имидазолидин)-2',5'-дитион.....	79
<i>П. П. Петрова, Ст. М. Милошев, Хр. П. Новаков</i> , Напречно свързани звездовидни съполимери, съдържащи ядро от С-тетра-алкилкаликс[4]резорзинарени.....	86
<i>Н. Маринов, М. Симеонова</i> , Получаване на полиетилцианакрилатни нановлакна чрез полимеризация в парова фаза с алкохолни инициатори.....	92
<i>В. Станева, Г. Иванова, М. Симеонова</i> , Повърхностно модифицирани поли-бутилцианакрилатни наночастици, натоварени с индометацин: получаване и физикохимично охарактеризиране.....	99
<i>И. Т. Спиридонов, Р.К. Боева, Т. Цв. Божкова, Я. В. Неделчев</i> , Изследване на влиянието на сумарното количество на мастилата в тъмните тонове (tas) върху точността на тоно- и цвето-възпроизвеждането при изображения отпечатани на ролен офсетов хийтсет печат.....	105
<i>П. Илиев, Вл. Стефанова, Б. Лучева</i> , Сярно-кисело автоклавно разтваряне на Ni-Co сулфидна утайка.....	111
<i>Б. И. Лучева, П. К. Илиев, Вл. П. Стефанова</i> , Извличане на сребро от цинкови кекове.....	117
<i>З. Главчева-Лалева, Л. Варадинова, Ст. Керекков, Д. Павлов, Ив. Главчев</i> , Приложение на отпадъчен глицерол от производството на биодизел за получаване на модификатор на триене на различни моторни масла.....	118
<i>Инструкция за авторите</i>	124