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Obtaining of Modifiers for Reduced Friction by Esterification of Waste Glycerol from Biodiesel Production and Sylfat 2

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Abstract The esterification of waste glycerol from biodiesel production (WG) ore pure glycerol (PG) with Sylfat 2 were made by catalyst 3% titanium alcoholate (TiAl) for 3 h at 150°C. The quantity of glycerol in WG and the oleic acid (OA) in Sylfat 2 were made with UV-VIS spectra. There UV-VIS and FTIR spectra were shown. Some quantity of free acids was neutralized with methylamine ore with 25% water solution of NH_3 and was given FTIR spectra of obtained products. All investigations for characteristics of these products were made with standard method by four ball machine. From WG ore PG and Sylfat 2 were obtained the valuable friction modifiers, comparable with standard compounds.

Keywords: *esterification, friction modifier, waste glycerol, biodiesel production*

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1. Introduction

The application of waste glycerol from biodiesel production was one of questions without correct answer. Because WG was obtained in all of world, that question was interesting for researchers from all countries. One possibility was production of fuels, but it was no interesting because the price of these products was no so high [1]. In [2,3,4,5] investigated the possibility for production of valuable chemicals. In all works were applied different microorganisms. It was known, that these technologies were connected with small spied of reaction and special equipments. The impurity in WG was very important and was problems for some technologies [6]. It was known that WG was the mixture of about: 50% glycerol, 8 – 10 % water, 4-7% soaps, 15 – 20% methanol, 1 - 3% alkalis, 10 – 15% biodiesel and fatty acids, 2% others. The production of friction modifiers were described in a lot of works. Those products were made from usual row materials. In this small synopsis was citrated only three of them – one world and two US patents [7,8,9]. In the last US patent was described friction modifier, made from Sylfat 2. This is the reason to work for application of that acid mixture for obtaining of valuables products by easy technologies. The esterification of Sylfat 2 with WG and with pure glycerol (PG) were made in the presence of a new catalyst – titanium alcoholates (TiAl), obtained for production of synthetic oils [10].

2. Experimental

The UV-VIS spectra were made of all applied materials with apparatus Cary 100 Scan UV-VIS spectrophotometer (Germany) in 10 mm covets. The spectra of waste glycerol (WG) and of pure – 99.9% glycerol (PG) were made in water solutions. The spectra of oleic acid (OA) and Sylfat 2 were made in toluene solutions. The applied OA and toluene, p.a. were products of Valerus Ltd, Bulgaria. The sample of Sylfat 2 was product of Arizona Chemical, USA. The applied PG was product of Spiga Nord, Italy. The FTIR were made in thin layer of all of investigated materials on the alkali plates with apparatus FTIR Varian (Germany). The FTIR spectrum of WG was made in thin layer on the plate, made from CaF_2 with apparatus FTIR Spectrometer Thermo Scietific Nicolet 6700. The esterification of Sylfat 2 with WG and PG with 3% TiAl were made for 3 h. in 150°C in glass reactor, supplied with steering. The catalyst TiAl was added like drops to the mixture of reagents, when the temperature was 150°C. In these reactions were made Products N 1 and N 2. The neutralization of free acids in Product N 1 were made in room temperature with alcohol solution of CH_3NH_2, p.a., product of Fluka, Germany and with technical grade 25% water solution of NH_3, product of Neochim Ltd. Bulgaria

and were made Products N 3 and 4. The wearing properties of the obtained products were determined by four ball machine in laboratories of University of Ruse "Angel Kanchev" at room temperature for 1 h., according method, described in БДС 9786 - 84. The values of Δ were calculated with equation:

$$\Delta_{inv.s.} = \%_{oil} - \%_{inv.s}$$

where $\Delta_{inv.s.}$ was the differences between $\%_{oil}$, (100) and $\%_{inv.s}$

The marcs in the ball were measured by prof. Pl. Kangalov from University of Ruse "Angel Kanchev" with microscope Dino-Lite Premier Digital Microscope AM-7013MZT.

3. Results and Discussion

The quantity and characteristics of WG was made by UV-VIS and FTIR spectroscopies.

In Figure 1 and Figure 3 were given the obtained spectra.

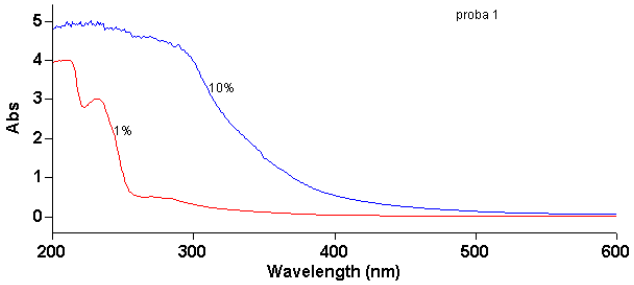


Figure 1. UV-VIS spectra of water solutions of WG

UV-VIS investigations of PG with 99.9% purity were given in Figure 2

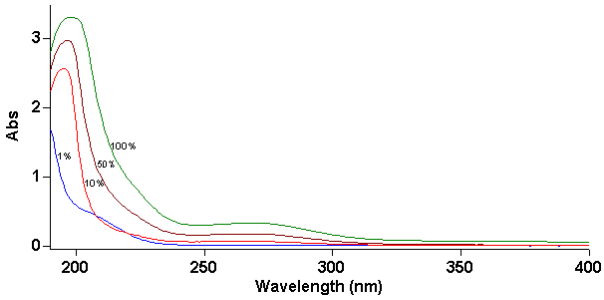


Figure 2. UV-VIS spectra of water solutions of 99.9% PG, p.a. made in Italy from Spiga Nord Ltd., Italy

From Figure 2 were made equations for dependences absorbance A / concentration C. Again like with G, p.a. of Valerus Ltd, Bulgaria the coefficient of correlation (R^2) in the band at 222 n.m. was bigger – 0,9985 and with this equation was made determination of concentration of G in WG. The value was 61.5%. The value, made with G of Valerus Ltd was 62% and was published in [11]. It was evident, that the difference between these values was very small. This is the reason to confirm that two concentrations were equal. The absorbencies of –OH, -CH-,-CH_2 in WG was at 3354.45 cm^{-1}, 2926.65 cm^{-1}, 2855.01 cm^{-1}, 1407.59 cm^{-1},1206.94 cm^{-1}, and were given in Figure 3.

It was known, that the plates of CaF_2 were available for investigation of water solutions, but did not given spectra under 1000 cm^{-1}. Because we did not information for kind of impurity in WG, we decide to make FTIR spectrum of this material in thin layer on the plate from CaF_2. The FTIR spectrum of PG was given in Figure 4.

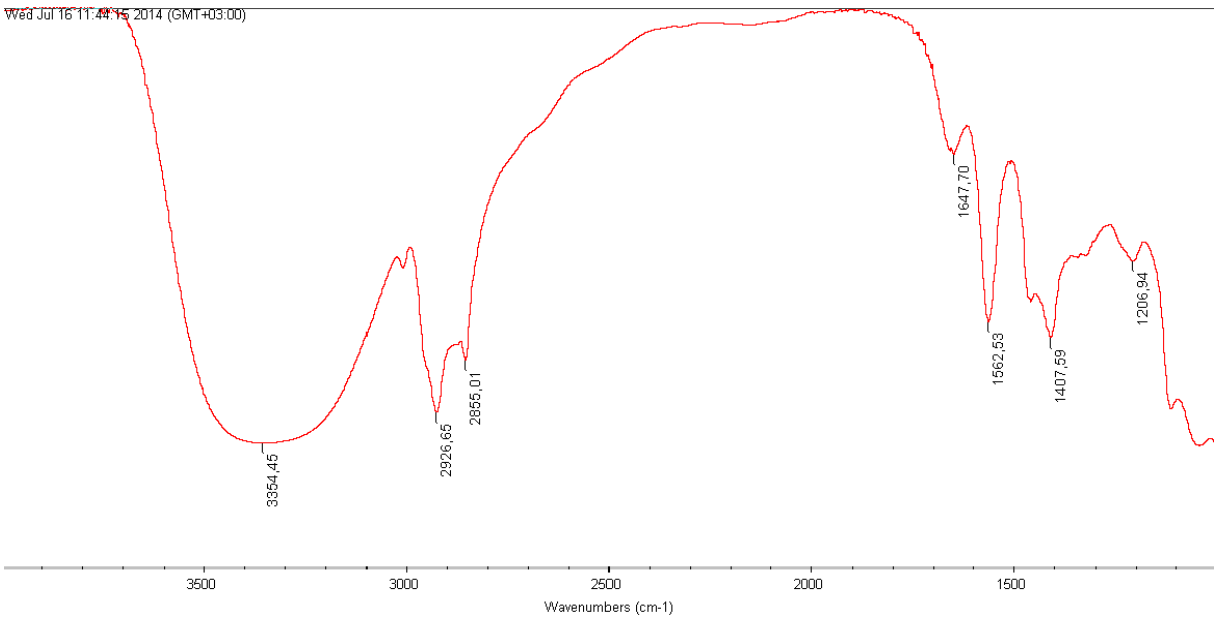


Figure 3. IR spectrum of WG in thin layer on the plate from CaF_2

The differences in the values of wave numbers of bands were results of obtaining of H bonds between G with impurities in WG. FTIR spectrum of applied PG was equal with IR spectra of glycerol, given in literature. The concentration of OA in the mixture of acids Sylfat 2 (a tall oil fatty acid with high fatty acid content and a low content of rosin acids and unsaponifiables) was given from the producer of that product to be 29%. The value of acid number (acid value) in the certificate of was minimum 194 [12]. We obtained with standard method for determination of those value [13] 241.8. This is the reason to made UV-VIS investigations with OA, p.a. product of Valerus Ltd, Bulgaria. The obtained results were in Figure 5.

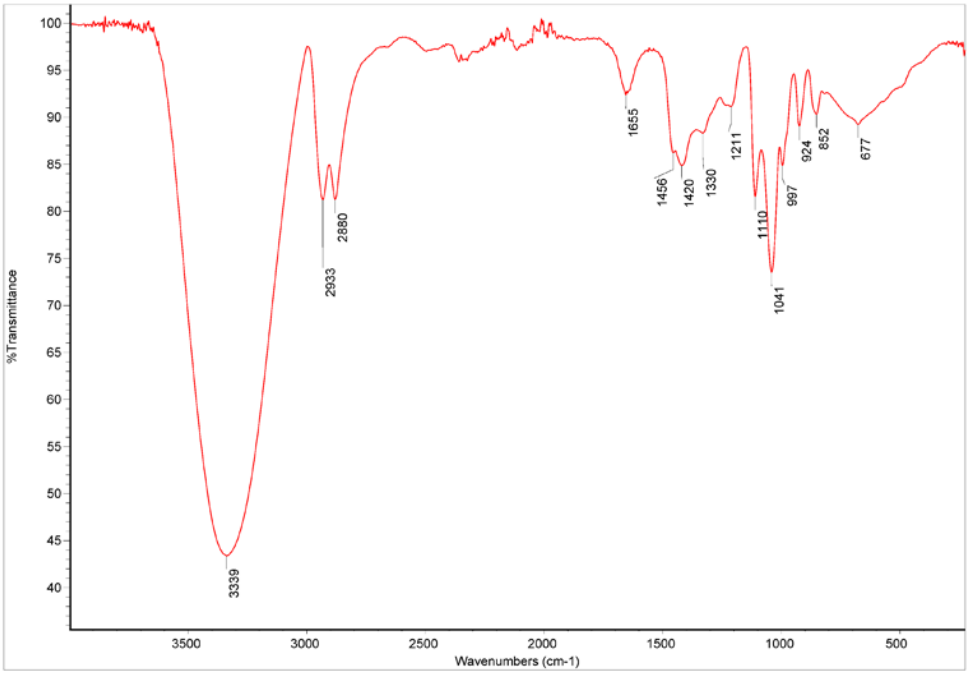


Figure 4. IR spectrum of PG made from Spiga Nord, Italy

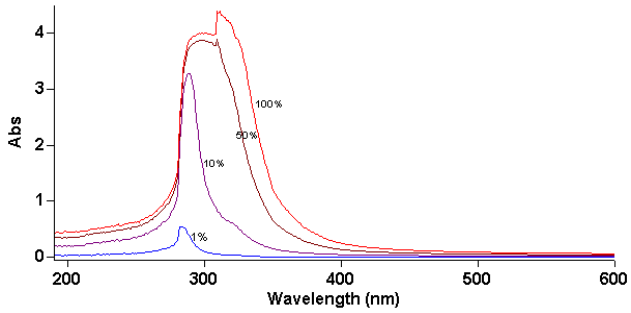


Figure 5. UV-VIS spectra of toluene solutions of OA

From Figure 5 were made equations for dependences absorbance A / concentration C. With the equation in 311 n.m. and with absorbance of Sylfat 2, given in Figure 6 was obtained the concentration of OA - 23.87%. The values of R^2 in the equation for 311 n.m. was bigger than 0.99.

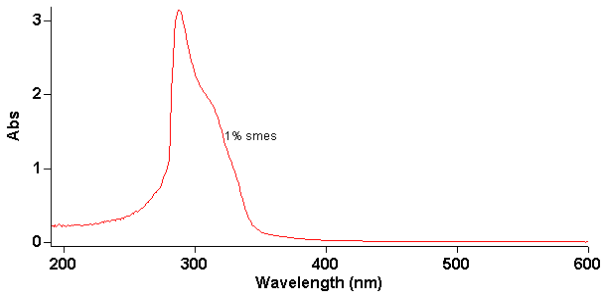


Figure 6. UV-VIS spectrum of toluene solutions of Sylfat 2

All UV-VIS investigations were made with known absorbance of toluene. The obtained value of OA corresponded with the value of acid number, measure in Bulgaria. Because in the literature we did not find the spectrum of that acid mixture (Sylfat 2), we decided to make FTIR spectrum of the sample, applied for experiments. FTIR spectrum was in Figure 7.

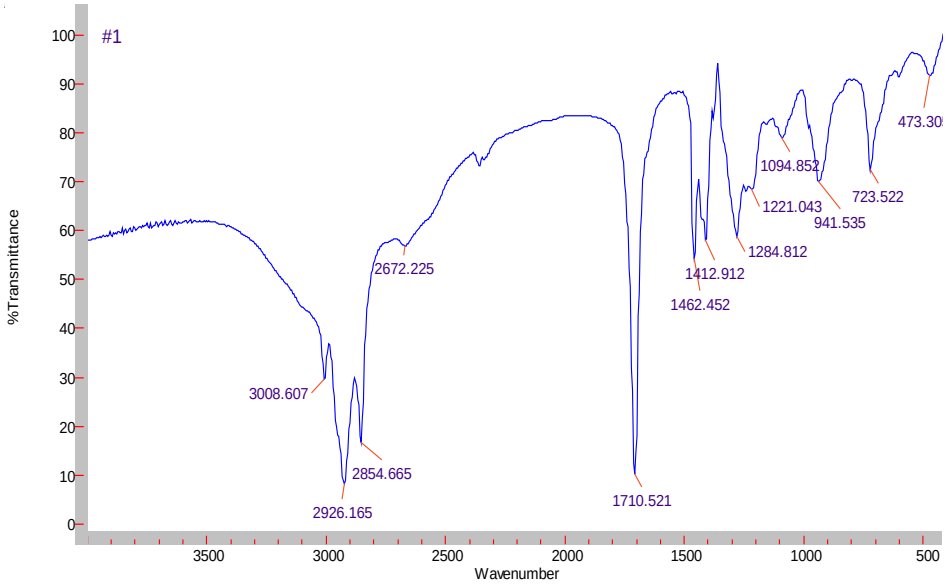


Figure 7. FTIR spectrum of sample of Sylfat 2, applied in experiments.

The content of fatty acids in that sample according producer was around 96%. We made esterification of Sylfat 2 with WG (Product N 1) and with PG (Product N 2) in the presence of catalyst TiAl 3% for 3 h. at 150^{0}C. The FTIR spectra of those products were in Figure 8 and Figure 9.

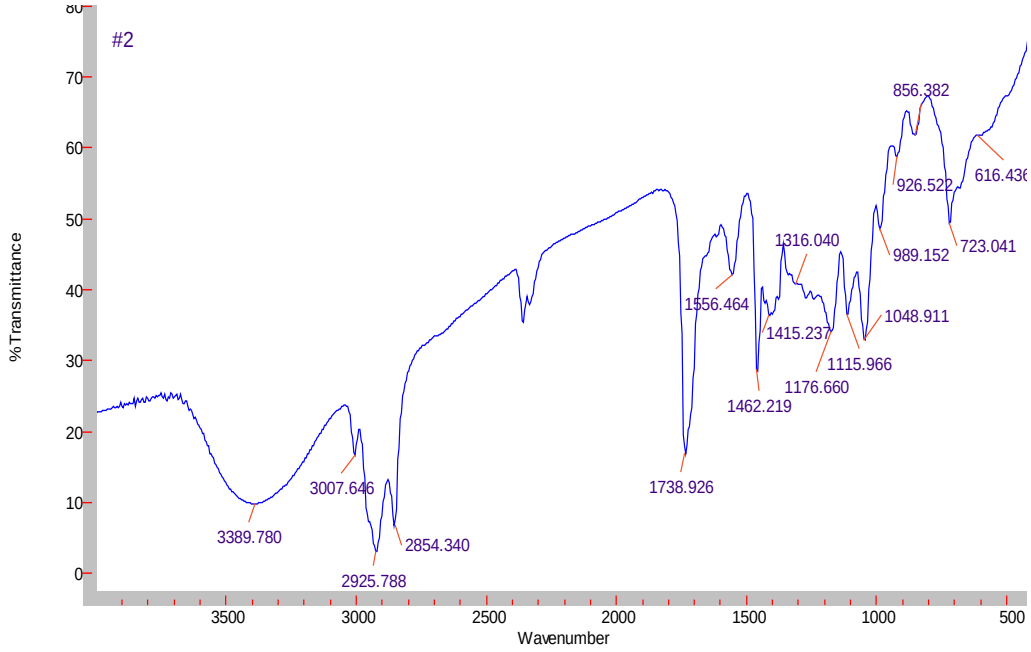


Figure 8. FTIR spectrum of Product N 1

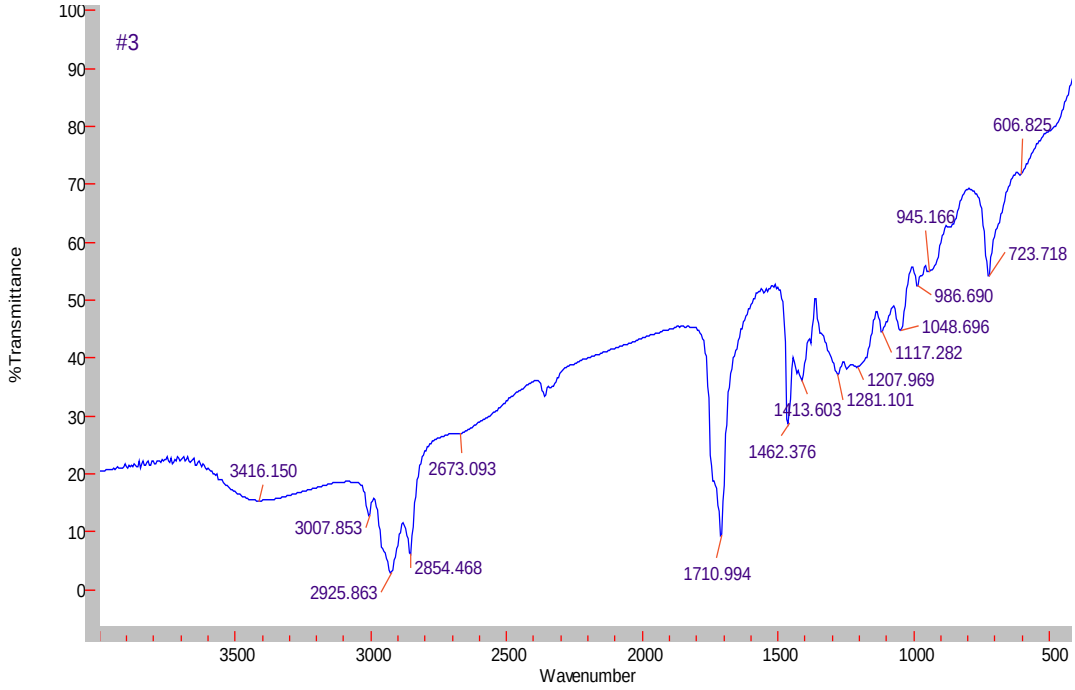


Figure 9. FTIR spectrum of Product N 2

It was clear, that row materials for production of this material were WG and Sylfat 2. In fig 9 was given FTIR spectrum of Product N 2.

The FTIR spectrum of this material have the band for C=O at the same wave number, like in Sylfat 2.

The neutralization of free acids in Product N 1 were made in room temperature with alcohol solution of CH_3NH_2, and with 25% water solution of NH_3 and were made Products N 3 and N 4, with FTIR spectra, given in Figure 10 and Figure 11.

The small content of free acid (small maximum for C=O group) was confirmed with determination of acid number of this material. The application of methylamine was evident by the bands for $–CH_3$ group. It was clear, that the neutralization of free acid was no made plenty in room temperature. It was necessary to apply a bigger quantity of methylamine, but after that was made vacuum distillation of free reagent.

From Figure 10 and Figure 11 were evident the differences in FTIR spectra of these materials. The application of 25 % water solution of NH_3 was inexpensive. All determination of friction reducing properties was made in standard mineral motor oil and was given in Table 1. The mineral motor oil $M10D_2/E_1$ was like standard mineral oil SAE 30 [13].

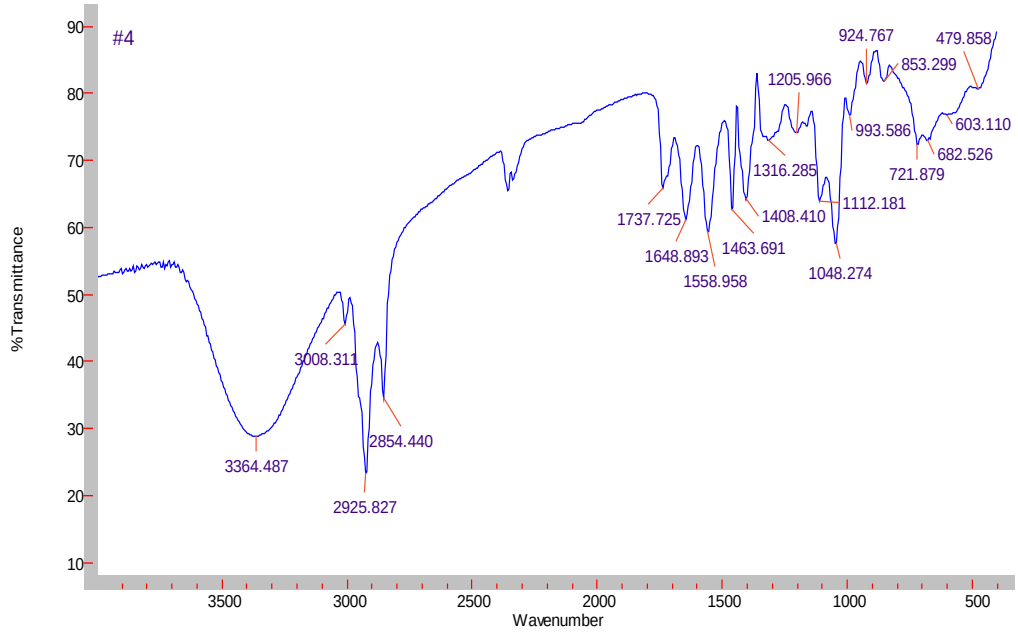


Figure 10. FTIR spectrum of Product N 3

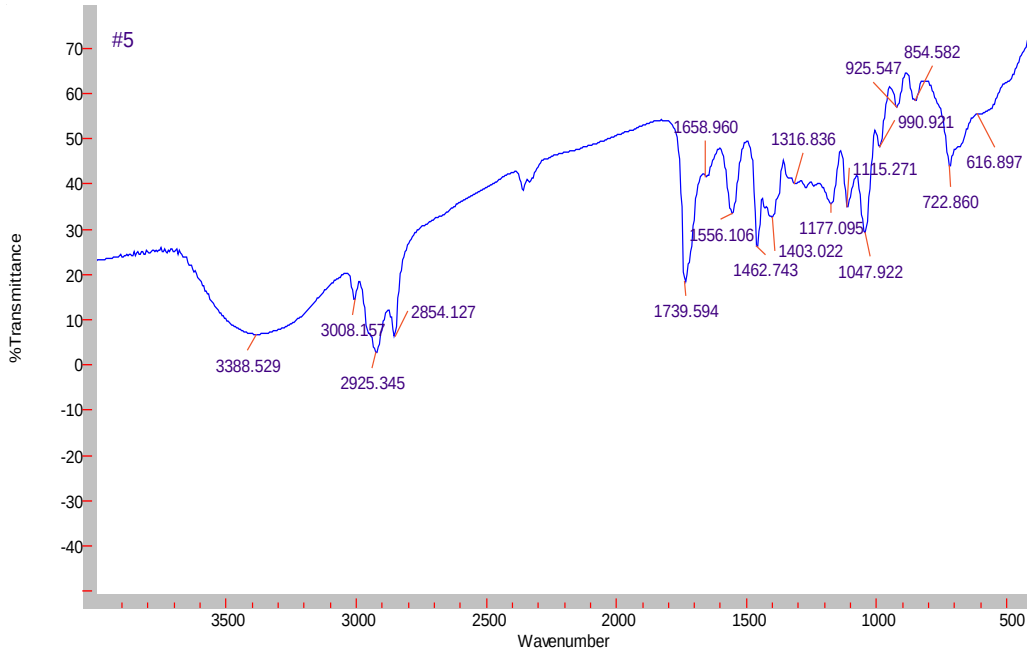
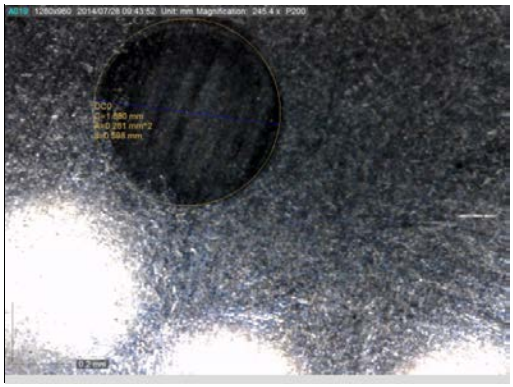


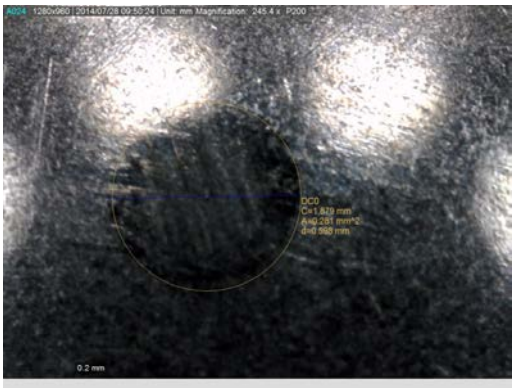
Figure 11. FTIR spectrum of Product N 4

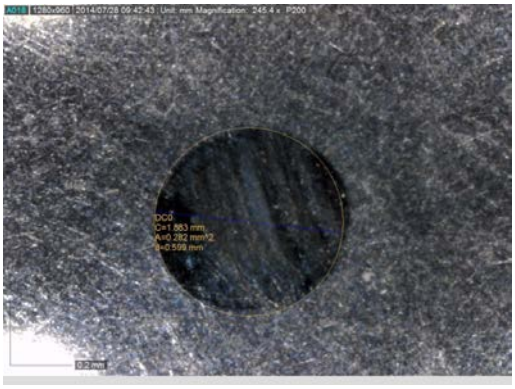
Table 1. Dependences between average diameter of wearing of the balls (d_{ave}), %, Δ from the quantity, % and the kind of investigated modifiers in motor oil $M10D_2/E_1$

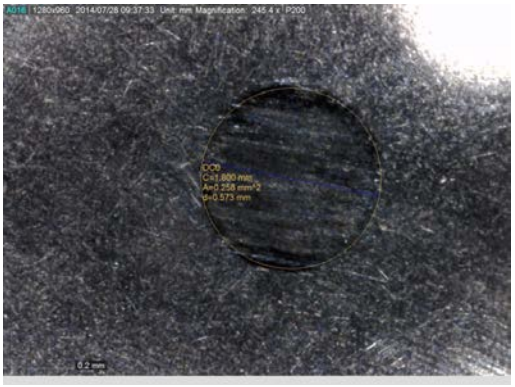
№	Quantity,% and the kind of modifier,	d_{ave} of wearing, mm.,%, Δ
1	0, Mineral motor oil $M10D_2/E_1$	0.61, 100, 0
2	2, Product N 1	0.571, 93.6, 6.4
3	0.5, Product N 1	0.574, 94.1, 5.9
4	2, Product N 2	0.589, 96.6, 3.4
5	0.5, Product N 2	0.596, 97.7, 2.3
6	2, Product N 3	0.582, 95.4, 4.6
7	0,5 Product N 3	0.603, 98.9, 1.1
8	2, Product N 4	0.561, 92, 8
9	0,5 Product N 4,	0,605, 99.2, 0.8
10	1, anylidoleate	0.60, 98.4, 1.6
11	0.5, anylidoleate	0.60, 98.4, 1.6
12	0.5, Zn oleate	0.60, 98.4, 1.6
13	0.5, Ti tetraoleate	0.60, 98.4, 1.6

Some of obtained marcs on the balls were given in pictures N 1, 2, 3 and 4. The all marcs have spherical shape with excellent borders and the making of mistakes in the measurements of their diameters was smaller.









From the results, given in Table 1 was evident that all samples were with better values, compared with the values of marcs of mineral oil $M10D_2/E_1$ and for standard friction modifiers. With the decreasing the quantity of the friction modifiers on the base of Sylfat 2 the values of d_{ave} increased. These results were in good agreements with theory of friction of motor oils. The values of Δ for 0,5% concentration of standards friction modifiers in the same motor oil (anylidoleate, Zn oleate, Ti tetraoleates) were smaller and this was the reason to determined, that investigated in this work friction modifiers from WG and Sylfat 2 were available for application.

4. Conclusion

The products, obtained in esterification of WG and PG with Sylfat 2 in the presence of catalyst TiAl were valuable friction modifiers of mineral motor oil.

Acnolidjement

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University of Ruse, 8 Studentska Str., 7017 Ruse, Bulgaria for measurements of the marcs on the balls after investigation with four ball machine.

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