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The Novelties Producing by Ozonolysis of Petroleum High-Molecular Components

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Abstract

Specific properties of ozonolysis products of high-molecular heteroatomic compounds (resins and asphaltenes) from crude petroleums and natural bitumens are described. It is shown that polyfunctional carboxylic acids or their salts obtaining by alkaline hydrolysis of ozonization products of heavy petroleum stocks permits to produce manifold useful novelties such as high-effective demulsifiers for petroleum dehydration process instead of expensive synthetic demulsifying reagents; water-soluble organic astringents suitable for chemical land-reclamation or to prepare moulding mixtures at the foundries; oily or emulsion lubricating coolants for metal-working tools; stimulators of soil microorganisms activity and plant growth. The new chemical products of petroleum origin are not inferior to the best synthetic reagents for the same destinations but differ from the lasts advantageously on account of the simplicity of their production technology and low cost.

The optimal expenses and other principal technological parameters were established both for raw material ozonization, following alkaline treatment and final product isolation stages of the production process for each new reagent described.

By means of numerous laboratory experiments and field tests performed with seeds, bulbs and grafts of different agricultural plants and with ozonolysis products produced from the resinous components of different crude petroleums it was proved that high biological activity is characteristic only of the substances obtained from high-molecular compounds from low-sulfur naphthenic crude petroleums and natural bitumens occurring, as a rule, at small burial depths. These ozonolysis products are very effective stimulants for the different plants growth, suitable for a treatment of different forms of planting materials and providing significant acceleration of early growth stages, the reduction of vegetation and ripening periods, and the increase of total productivity of agricultural plants.

Introduction

Ozone is an exceptionally reactive chemical agent capable of fast interactions with a variety of organic compounds, including petroleum heteroatomic components and polycyclic aromatic hydrocarbons [1,2]. The specific properties of resultant substances open up wide possibilities for working out novel technological processes and manufacturing new products, which may find useful application in various fields of economy [3].

The main products of oil-stock ozonization process carried out in hydrocarbon or other non-alcoholic media are cyclic peroxides (ozonides) forming as a result of ozone addition to C-atoms joined by unsaturated C=C bonds in molecules of condensed polycycloaromatic compounds. The oxidation of petroleum sulfides into sulfoxides and further into sulfones is an important reaction readily proceeding on ozonization of high-sulfur raw materials. When an ozonation of crude petroleums, petroleum fractions or solutions of petroleum residues, resins and asphalthenes is carried out as a slow prolonged (1-2 h) process, the oxidative destruction reactions of ozonides to give mainly dicarboxylic acids as well as radical-chain oxidation reactions of raw-stock components initiated by ozone develop.

Both ozonides and sulfoxides are thermally unstable substances which destroy readily being heated

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up to 110-120°C and above and can serve as initiators of low-temperature radical-chain cracking reactions of all petroleum components [3,4]. These reactions can be used for initiated low-temperature destruction of heavy petroleum ends to produce additional amounts of motor distillate fractions [5,6]. An analogues low-temperature thermo-destructive approach was used when the ozonization process became the method of new lubricating coolants production [7].

Well-known another way to break up ozonide molecules is their alkaline hydrolysis leading to different substances enriched in oxygen and having manifold useful properties. The means of production and the properties of reaction products are the principal objects of this our short communication.

Experimental

Depending on concrete purpose, the different crude oils, their heavy ends or hydrocarbon solutions of petroleum resins and asphaltenes were ozonizated in the reactors of ebullition or through-flow type at the temperature of 20-90°C, hand-picked from considerations of a viscosity of ozonizating liquid would be no more than 20 cs, but simultaneously it would be not above the temperature of break-up of ozone molecules. When crude oil ozonization to produce reagent-demulsifier, resulted reaction mixtures were the products ready for use. In the most rest cases the reaction products were mixed thoroughly with NaOH or KOH solution in water (concentration about 5 wt.%) at 90-95°C, then water phase of the system was separated, and the final ozonolysis product was isolated after water distillation and air-drying and tested as appropriate.

In more detail methodical and analytical aspects of the investigations and tests will be described below for each of particular cases.

Results and Discussion

Owing to presence of hydrophilic functional groups, especially COOH ones, and of large-scale hydrophobic saturated fragments (alkyl chains, polycyclic naphthenic systems), the molecules of ozonolysis products of petroleum high-molecular compounds (PHMC), the last being mostly resinous substances, exhibit strongly pronounced surface-active properties and can be used as high-effective *demulsifying reagents* for crude oil dehydration processes.

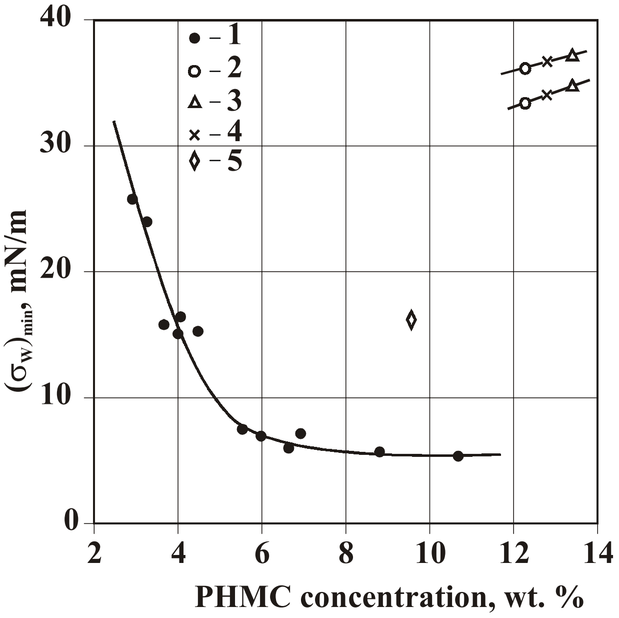
It was shown that hydrolyzed by alkali ozonization products (HOP) of petroleum high-molecular components are not inferior to the best synthetic reagents in their surface activity and demulsifying properties. So, by adding 0.01 wt.% of such ozonization products to West-Siberian crude oils the interphase tension σ_w on their boundary with fresh water (pH 7.0) is lowered down to the values less than 0.03 mN/m, while an addition of even 0.04 wt.% of such widely using industrial reagents as Dissolvan 4411 or Separol WF-44 results in σ_w value decrease only down to 10-12 mN/m [5].

New demulsifying agents are easily obtainable under oil-field conditions via direct ozonization of crude oils as natural hydrocarbon solutions of resins and asphaltenes. The method of oil dehydration based on the above process has been worked out [6]. The tests carried out under laboratory and field conditions with model and native water/oil emulsions have confirmed high efficiency of the method suggested.

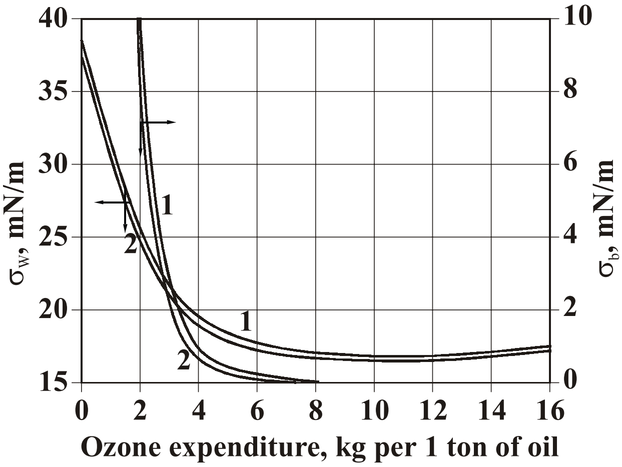
The principal trends in the interphase and demulsifying activity of these reagents as a function of crude oil composition and of oil treatment conditions were established, and optimal process parameters were determined with respect to oils from various fields of Turkmenistan, West Siberian and Volga-Ural regions. The optimal ozone expenditure was found to exist for each crude oil, at which the minimal σ_w value on oil/water boundary is reached. At greater ozone expenses, a part of organic acids formed combines the hydrocarbon-insoluble associates ceasing to serve as surface-active compounds.

Both optimal ozone expenditure and minimal σ_w $(\sigma_w)_{min}$ values depend significantly on petroleum composition. To obtain most effective demulsifier, only 7-10 g of O_3 per 1 kg of petroleum should be spent when treatment high or gently resinous West-Siberian crude oils (see Fig. 1). At that cases, $(\sigma_w)_{min}$ values come to 4.5-7.5 mN/m. More less effective reagents were obtained from low-resinous crude oils of the same province: they were able to reduce $(\sigma_w)_{min}$ values only down to 15-16 mN/m (lower Cretaceous petroleums) or even to 22-24 mN/m (Jurassic ones), so as to produce more active demulsificators one has to increase the specific ozone expenditure up to 12-16 g/kg.

The most difficult task is to make active demulsifying agents from very high sulfurous oils, for example, from ones extracting at Bashkirian and Permian fields and containing up to 5-6 wt.% of sulfur, mostly in sulfide form. It is obvious that at these cases sulfoxides, which are possessed of weak base properties



Oil-producing provinces: 1 – West-Siberia; 2 – Bashkortostan; 3 – Perm region; 5 – Turkmenistan.
Fig. 1. Minimal interphase tension values on the boundary between ozonizated petroleum and fresh water depending on PHMC content in the raw material.



Oil ozonization temperature: 1 – 75°C; 2 – 90°C.
Fig. 2. The changes of interphase tension values on the boundaries between ozonizated Turkmenian petroleum (Kamyshlja oil-field) and fresh water (σ_w) or alkaline buffer solution (σ_b) depending on ozonization process intensity and temperature.

in hydrocarbon media, react with acids forming simultaneously during ozonization process making surface-inactive organic salts.

As it was shown earlier, the organic (carboxylic) acids have the strongest surface activity among all native petroleum heteroatomic components [7]. Similarly, poly-functional acids forming by crude oil ozonization process are the main surface-active components of reaction mixtures obtained. Therefore, HOP behave themselves as surface-active substances (SAS) of anionic type whose effectiveness became fully apparent when adjacent water phase has alkaline reaction (pH > 7.0).

In fact, after slight alkalization of oil/water emulsion subjecting to separation by increasing pH value of water phase only up to 7.62 (buffer solution of $Na_2B_4O_7$ + HCl) the surface tension on the interphase boundary declined by two-three orders, down to $\sigma_b < 0.02$ mN/m, *i.e.* to the values not accessible to measurement by means of stalagmometric method (see Fig. 2).

The optimal ozone expenditure amounted only about 6 g/kg instead of almost 9 g/kg when water phase of the emulsion did not contain alkali addition.

The laboratory model experiments and field testing of real extracted oil/water emulsions showed that the process described provides practically complete dehydration of crude oil under the same conditions (temperature, duration) which are usually in use at industrial units.

Furthermore, as a result of wide and diverse functional composition of their molecules, PHMC ozonolysis products are capable of strong adhesion onto metal and mineral surfaces and so can be used as effective additives useful to manufacture cutting lubricants for metal-working and chemical reagents for anchoring and hardening of dry materials.

The mineral lube oils containing the additions of such polar organic substances as carboxylic acids and their esters, organic sulfurous compounds ea. as well as the emulsions of these oily solutions with water (emulsols) are usually in use for lubricating and cooling of cutting instruments at metal-working plants [8]. The PHMC ozonolysis products can play successively the role of such polar additives, which was proved experimentally [9].

In these experiments, the solutions of 10-20 wt.% of natural bitumen (Mortuk field, Kazakhstan) or residuum from West-Siberian petroleum boiling above 540°C (goudron) in straight-run oily distillates or even in waste mineral lube oils having wanted viscosity were ozonized, then heated up to 150-180°C for ozonide destruction and exposed to hot filtration for eliminating solid intermolecular associates formed. As a result, ready for use very effective *cutting lubricants* for metalworking were taken out.

The tests performed at Tomsk instrumental plant revealed essential advantages of these new materials in comparison with the similar technical liquid of MR-7 grade consisting of 80% of sulfurizated industrial oil and 20% of vegetable oil and using industrially for the same purpose, as it is obviously seen in Table 1.

Table 1

Some results of tests performed when manual-threading openings bored in the cutters using industrial lubricant of MR-7 grade or goudron-oil mixture ozonolysis product

Cutting lubricant	Amount of goudron dissolved, %	Ozone expenditure, g/kg of goudron	Yield of product, % on initial oil solution	Number of holes treated by one tap
MR-7	-----	-----	-----	80
Ozonolysis Product	15.0	133	94.5	370
	18.0	160	93.2	340
	10.8	174	97.4	364

Unlike MR-7 liquid permitting to thread only 80 openings in the cutters made up of very hard stainless steel before an abrasion of cutting tap, the cutting lubricants obtained by ozonolysis of goudron-oil solutions make it possible to perform 340-370 similar operations without any notable wear of the same cutting instrument. In other words, wear resistance of the metal-cutting instruments can be increased by three-four times and more by using the new cutting lubricants suggested.

Two possible applications of hydrolyzed ozonization products (HOP) obtained from petroleum HMC or residues based on their ability to strong adhesion to the surfaces of mineral materials were also suggested. That was their using as soil-structuring agents [10, 11] and water-soluble mould and core binders for casting processes [12].

It was found that by introducing the HOP into heavy loamy soils in amount of several tenth fractions of a percentage the significant lumping (structuring) of clay components occurs, *i.e.* the content of coarse-grained particles in the mineral material rises. This makes it possible to use the HOP as high-effective water-soluble organic *astringents for land-reclamation* works.

Jointly with the specialists from the Institute of agricultural chemistry and soil science (Siberian Branch of Russian Academy of Sciences, Novosibirsk) we studied the soil-structuring properties of HOP obtained by ozonization of resins isolated from crude oil of Russkoe field (Tyumen region) and further boiling the reaction mixture with water solution of KOH [3,8]. The final HOP obtained in the yield of 69.2 wt.% were introduced into gray timber soil samples extracted from the layers of 0-20, 20-40 or 40-60 cm from day surface level.

These soil samples were grinded, bolted to separate the lumps larger than 3 cm in diameter, thoroughly mixed with calculated volume of water solution containing 1.0 or 0.1 wt.% of HOP and then dried to air-dry state. The distributions of initial and treated soil grains by size were measured by sieving method. For comparison, the similar experiments were performed with using partly hydrolyzed polyacrylamide (reagent K-4) recommended earlier to use for the same soil-structuring purpose [13]. Some data obtained are given in Table 2.

These experiments showed that by adding 0.1-0.2 wt.% of PHMC ozonolysis products a number of large-sized grains (> 1.0 mm in diameter) in the soil samples tested can be augmented by 5-6 times in arable and by 10-20 and more times in sub-arable soil layers. A comparison of total amounts of particles sized > 0.25 mm in diameter formed owing to using two reagents registered in Table 2 indicated that products of petroleum origin resulting by ozonolysis process are only a little inferior to synthetic water-soluble polymer by their soil-structuring action.

It is of great importance that by proper choice of an initial raw stock (*i.e.* chemical type of original petroleum) it is possible to produce HOP having good soil-structuring properties and simultaneously capable of stimulating the vital activity of soil microorganisms. This energization of the bacteria becomes apparent due to significant increase of carbon dioxide content in the soil air up to 2-3 vol.%, continues

Table 2
The changes of macro-aggregate composition of gray timber soil caused by introducing different amounts of HOP or K-4 reagents

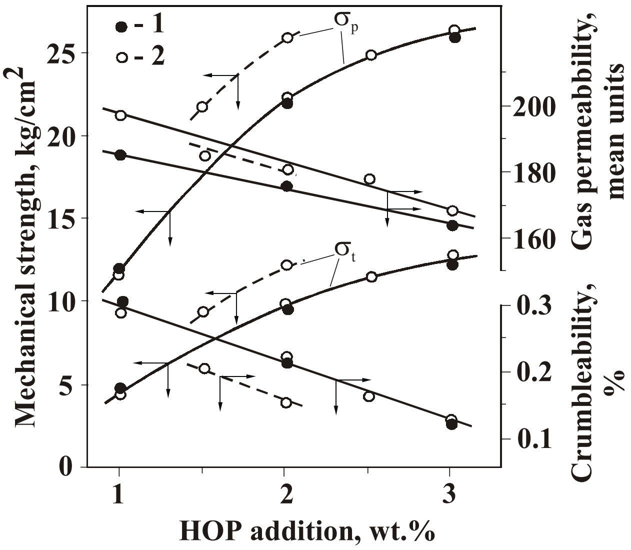
Reagent, its quantity added	Fraction of grains sized, mm, in diameter			
	> 1.0	1.0-0.5	0.5-0.25	> 0.25 in sum
Soil from 0-20 cm layer				
-----	6.4	11.7	15.1	33.2
HOP, 0.20%	37.3	18.8	19.2	75.3
HOP, 0.10%	31.6	10.2	11.6	53.4
HOP, 0.01%	2.1	4.3	10.2	17.1
HOP, 0.001%	1.9	4.9	8.8	15.5
Soil from 20-40 cm layer				
-----	1.3	3.2	15.8	20.2
HOP, 0.20%	22.1	16.8	16.5	55.4
HOP, 0.10%	13.2	9.4	10.7	33.3
HOP, 0.01%	1.8	2.4	7.1	11.3
HOP, 0.001%	1.1	2.0	7.0	10.5
Soil from 40-60 cm layer				
-----	0.1	0.9	4.1	5.1
HOP, 0.20%	44.0	7.1	6.3	57.4
HOP, 0.10%	44.5	5.6	4.3	54.4
HOP, 0.01%	0.04	0.3	1.9	2.2
HOP, 0.001%	0.02	0.4	2.1	2.4
Soil from 0-20 cm layer (by data of [13])				
-----	-----	-----	-----	37.2
K-4, 0.20%	-----	-----	-----	81.2
K-4, 0.10%	-----	-----	-----	74.3
K-4, 0.05%	-----	-----	-----	56.3

for two-three weeks after reagent introducing and is most noticeable in the soils poor in organic substances.

The criteria of the choice the petroleum that can be source of such biologically active PHMC ozonolysis products are given below.

Furthermore, it was found that by mixing of quicksand with 1-3 wt.% of the same PHMC ozonolysis products, then moistening the mixture with small amount of water and finally complete drying leads to its solidification. Owing to this effect HOP described can serve as high-quality water-soluble organic *astringents for preparation moulding mixtures* at foundries [12]. As such astringents, HOP provide great mechanical durability of cores and moulds, namely pressure strength of 26-28 kg/cm^2 and tensile strength of 12-14 kg/cm^2 when up to 3.0 wt.% of HOP was added to the sand, see Fig. 3, while sufficient values are almost half [14].

The gas permeability and crumbleability (weight losses because of crumbling) of moulds and cores obtained also were completely satisfactory. Additional merits of these wares were easy extraction of castings made, an absence of burnt-on sand and, especially, the possibility to regenerate and reuse moulding earth and non-burnt part of organic additives. The characteristics of moulds prepared on the base of regenerated sand are also shown in Fig. 3 by stroke lines.



σ_p – pressure strength, σ_t – tensile strength
Fig. 3. Physico-mechanical properties of the moulds containing HOP as an astringent and prepared with using fresh (1) or regenerated (2) quicksand samples.

Using the moulds and cores prepared from moulding mixtures containing above amounts of the astringents described high-quality castings from aluminum, brass, cast-iron and steel were made.

As it was said above, PHMC ozonolysis products can to strengthen significantly the vital activity of soil microorganisms as well as to stimulate a growth of agricultural plants. This biological activity is peculiar to not at all these substances, but only to reagents produced from some correctly selected sorts of initial crude oils. To determine the rules of the selection, we studied the biologically active properties of HOP produced by ozonolysis from resinous components of several crude oils and natural bitumens differing essentially by their chemical composition [3,15,16].

The biological activity of native petroleum components and products of their chemical modification is known for a long time. Its manifestations are different and can be either positive (stimulating) or negative (inhibiting he organism growth). The petroleum of Naftalan field using in pharmaceutical practice may serve as the example of natural substance showing the positive effect.

There were known petroleum growth substances (PGS), which were the wastes of alkaline refining of middle petroleum distillates [17]. These PGS possessed high but unfortunately, not permanent bio-stimulating activity. The absence of full information about chemical structure of these substances and reliable control of the stock composition was the main cause of the instability of PGS testing results. The process for producing plant growth stimulants via an oxidation of water-alkali-ne peat suspension by ozone-air mixture was also described [18], but oxyhumates obtained had still less biological activity than PGS.

We have found that the potassium salts of organic acids generating be ozonolysis of PHMC from some crude oils and natural bitumens are much more powerful stimulants of plant growth. The tested were HOP's produced from resinous components of following natural sources.

1. Very low-sulfurous (< 0.2 wt.%), resinous (7.1 wt. % of HMC), non-paraffin, sharply naphthenic by hydrocarbon composition, Cenosoic crude oil of Troitskoe oil-field (Krasnodar region, Russia, burial depth less than 200 m);
2. Low-sulfurous (0.35 wt.%), high-resinous (up to 17 wt.% of HMC), non-paraffin, sharply naphthenic by hydrocarbon composition upper Cretaceous crude oil of Russkoye oil-field (Tyumen region, Russia, burial depth of 880 m);
3. Sulfurous (0.8 wt.%), resinous (7.2 wt.% of HMC), methane-naphthenic lower-Cretaceous petroleum of Samotlor oil-field (Tyumen region, 2100 m);
4. High-sulfurous (4.8 wt.%), very high-resinous naphthenic upper-Cretaceous crude oil of Kokaity field (Tajikistan, 1180 m);
5. Natural bitumen from Iman-Kara field (West Kazakhstan, Aptian, occurrence depth less than 25 m, S content – 0.85 wt.%, HMC content – 63 wt.%, paraffin is absent).

Ozonizated in these experiments were cyclohexane solutions of petroleum resins. After completion of the process the settled precipitates ("ozonides I") were filtered, cyclohexane was distilled off from the filtrate and "ozonides II" were obtained as the residue. The substances I and II were separately hydrolyzed by heating with KOH solution at 90-100°C for 30 minutes, then water-alkaline solutions were acidified be diluted hydrochloric acid down to pH 1-2, the formed organic acids I and II were isolated and washed on the filter by water to the neutral reaction of the filtrate. The final acidic products I and II were the powders of dark-brown colour; their yields and general features are given in the Table 3.

Table 3

General characteristics of petroleum resins and acidic products of their ozonolysis

Oil-field	O_3 exps., g/kg	Product	Yield,wt.%	Molecular mass, a.e.m.	Content, wt.%, of				
					C	H	N	S	O
Troitskoye	68	Resins	100.0	780	85.40	10.21	1.52	0.81	2.06
		Acids I	69.3	598	75.89	10.46	0.65	0.37	12.63
		Acids II	45.2	532	80.79	10.51	0.84	0.32	7.54
Russkoye	83	Resins	100.0	1020	85.77	9.92	1.45	1.16	1.69
		Acids I	67.2	640	71.98	8.48	0.40	1.16	18.00
		Acids II	49.0	480	78.67	10.20	0.65	1.10	9.38
Samotlor	87	Resins	100.0	870	82.08	9.83	0.30	2.09	5.70
		Acids I	77.9	710	64.45	6.92	1.07	2.76	24.80
		Acids II	62.1	495	65.35	8.73	0.36	2.01	23.65

Table 3
Continued

Oil-field	O_3 exps., g/kg	Product	Yield,wt.%	Molecular mass, a.e.m.	Content, wt.%, of				
					C	H	N	S	O
Kokaity	146	Resins	100.0	1370	79.27	9.78	1.12	7.47	2.36
		Acids I	76.8	1140	66.19	8.16	1.23	7.60	16.82
		Acids II	47.2	950	78.88	9.73	0.67	2.43	8.29
Imankara	74	Resins	100.0	1115	81.42	9.60	0.60	0.80	7.58
		Acids I	64.2	745	71.07	8.38	0.61	0.84	19.10
		Acids II	50.3	660	79.17	9.34	0.43	0.62	10.44

The acids I and II were repeatedly dissolved in KOH-water solution so as to increase pH value up to 8-9, then water was evaporated and the products were dried in the vacuum box. The obtained powder-like substances well dissolving in water are named further *Lesikats* T-1, T-2, R-1, R-2 and so on (the designations are by first letters of field names).

At preliminary laboratory testings the seeds of different plants were soaked in *Lesikat* solutions with 0.001-0.01 wt.% concentrations in Petri dishes for different periods of time, then the solutions were drained? The seeds were dried a little, wetted by water and germinated in darkness at room temperature for several days. Four days later and each following day in future the lengths of roots and stalk sprouts were measured. In analogous control experiments distilled water was used for the steep of seeds instead of *Lesikat* solutions. All experiments were repeated 3-5 times and the results were averaged.

The testings with corn and garden radish seeds has shown strong dependence of *Lesikat* biological activity on the chemical nature of the crude (see Table 4).

There were found powerful biostimulating properties of *Lesikats* produced from resinous components of Iman-Kara bitumen, the petroleum of Russkoye and, especially, of Troitskoye oil field. Cyclohexane-soluble *Lesikats* were in all cases more active than the products precipitated from this solvent. *Lesikats* S-1 and S-2 from Samotlor petroleum resins were found almost inert biologically, while the products resulted from the resins of Kokaity crude oil were inert (K-2) or, in contrary, depressed a plant growth (K-1).

Comparing the Table 3 and desk 4 data it is easy to observe strong antibathical relationship between the *Lesikat* activity levels and its sulfur content. These results allow to suppose that the greatest bio-stimulating activity is characteristic of forming by ozonolysis oxygenic compounds containing no sulfur and having, more probably, the polycyclane skeleton of molecules, sulfur-bearing conversion products apparently inhibiting the plant growth. It follows that to obtain high-effective bio-stimulants by the method described it is necessary to use resinous components from low-sulfurous crude petroleums and natural bitumens of distinctly naphthenic hydrocarbon type as raw material.

Table 4
Growth of roots and stalks of garden radish and corn when their seed sprouting in water after six-hour soaking in 0.01% solutions of different *Lesikats* (control – 100%)

Reagent	Relative length (%) of			
	Roots	Stalks	Roots	Stalks
	of garden radish		of corn	
T-1	280	265	245	230
T-2	470	390	330	375
R-1	180	195	110	140
R-2	210	235	170	155
S-1	105	115	100	105
S-2	110	105	105	100
K-1	40	80	85	95
K-2	105	115	90	100
I-1	170	230	170	210
I-2	275	245	120	280

In analogous experiments with seeds of corn, cucumber, tomato and cotton treated with R-2 Lesikat solutions the noticeable concentration dependence of effects observed was found (Table 5). Thus, when the reagent content in the solution was increased from 0.001 to 0.01 wt.% the effect of stimulation of corn, tomato, cotton root growth became stronger while for cucumber, on the contrary, it became some weaker that showed to individual reaction of seeds of different plants.

Table 5

Acceleration pf root growth after seed soaking in R-2 *Lesikat* solution (control – 100%)

Concentration of *Lesikat* in water solution, wt.%	Relative length (%) of roots (%) for			
	corn	cucumber	tomato	cotton
0.001	126	137	150	104
0.01	153	124	158	128

A host of examples of successful laboratory experiments and more extensive field tests of *Lesikats* to stimulate the germination and further vegetation and ripening of many different plants were presented in our publications [15,16]. Described were the cases of *Lesikat* treatment not only of seeds, but also of bulbs (gladiolus) and grafts (rose).

Our data witness convincingly that the ozonolysis products produced from resinous components of low-sulfur naphthenic crude petroleums and natural bitumens occurring, as a rule, at small burial depths, can serve as very effective stimulants for the different plants growth, suitable for a treatment of different forms of planting materials and providing significant acceleration of early growth stages, the reduction of vegetation and ripening periods, and the increase of total productivity of agricultural plants.

There are all reasons to believe that the ozonolysis of petroleum components and the products of this very effective process will find new promising applications in the nearest future.

Conclusions

The ozonization of petroleum high-molecular compounds following with alkaline hydrolysis of the reaction products is very perspective way to produce the various chemical reagents possessing useful properties for different practical applications.

The hydrolyzed ozonization products (HOP) of petroleum high-molecular components can be used as high-effective demulsificators for crude oil dehydration processes. These reagents of anionic type are not inferior to the best synthetic substances in their surface activity and demulsifying properties.

The mineral lube oils containing the additions of PHMC ozonolysis products as well as the emulsions of these oily solutions with water (emulsols) can serve as very effective lubricating coolants for metal working. The wear resistance of metal-cutting instruments can be increased by three-four times and more by using the new cutting lubricants suggested.

Strong adhesion of HOP onto the surfaces of mineral materials makes it possible to use these reagents as effective water-soluble organic astringents for land-reclamation works, for anchoring and hardening of dry materials. By proper choice of the chemical type of original petroleum, it is possible to produce HOP having good soil-structuring properties and simultaneously capable of stimulating the vital activity of soil microorganisms.

Owing the same adhesive properties the reagents described can serve as high-quality water-soluble organic astringents for preparation moulding mixtures at foundries.

The ozonolysis products produced from resinous components of low-sulfur naphthenic crude petroleums and natural bitumens occurring at small burial depths are very effective stimulants for the different plants' growth, suitable for a treatment of different forms of planting materials and providing significant acceleration of early growth stages, the reduction of vegetation and ripening periods, and the increase of total productivity of agricultural plants.

We hope that new ozone technologies will rank worthy high among other traditional petroleum refining processes as well as new petrochemicals described here will be widely adopted in the different above mentioned economical fields.

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