The Present State of Research into Organosulphur Compounds in Petroleum

1982 Russ. Chem. Rev. 51 189

(http://iopscience.iop.org/0036-021X/51/2/R07)

Russian Chemical Reviews, **51** (2), 1982

Translated from *Uspekhi Khimii,* 51 332-354 (1982)

U.D.C. 547.26/27 + 547.73 : 665.61 + 665.65

The Present State of Research into Organosulphur Compounds in Petroleum

N.K.Lyapina

Data on the compositions, structures, and properties of organosulphur compounds forming part of various petroleum distillates are examined. Attention is concentrated on the organosulphur compounds in high-boiling petroleum distillates. The results of studies on the individual and structural-group compositions of mercaptans, sulphides, and thiophens in various distillates of typical petroleums of the USSR are presented. Certain chemical properties of the organosulphur compounds of petroleum and the problems of their utilisation in the national economy are discussed.
The bibliography includes 114 references.

CONTENTS

I. INTRODUCTION

Organosulphur compounds, which have found extensive applications both in large-scale technical chemical processes and in fine organic synthesis, have been vigorously and comprehensively investigated in recent years. Natural organosulphur compounds (OSC) of petroleum origin, which consist of sulphides, thiophens, and mercaptans of different structure and molecular weight, have a wide spectrum of specific properties and can serve as starting materials for the synthesis of polyfunctional, bi- and poly-dentate compounds with still more interesting properties. It is sufficient to mention that sulphides from petroleum can be used as effective extractants for noble metals and that the sulphoxides obtained from them are highly selective extractants of many heavy metals and lanthanide elements.

However, in modern processes for the purification of petroleum products the OSC are either converted into hydrocarbons and hydrogen sulphide, or they are transformed into acid resins, or they remain in the petroleum products; in all these instances they are lost for specific applications. One of the main factors hindering the wide-scale employment of the OSC in the national economy is inadequate knowledge of their structure and properties. The interest in these compounds, which has arisen since the discovery of sulphurous petroleums, has been growing and expanding; the methods for the isolation and study of the composition of the sulphides and thiophens in individual petroleum distillates as well as data on their structure have been surveyed in reviews and monographs[1-3].

The studies in recent years (since 1975) are characterised by a combined approach to the investigation of the composition and properties of the OSC in petroleums and by an endeavour to determine the structure of the OSC of the entire distillate component of petroleum and to extend the practical applications of the OSC. Much attention has been devoted to the study of the OSC in high-boiling distillates, because the main bulk of the petroleum OSC is concentrated in the latter. These results are of considerable theoretical and practical interest for both petroleum chemistry and for the improvement of the technology of the processing of petroleum in order to increase the yield of light petroleum products. The study of the structure and properties of the OSC not only makes it possible to find applications for these substances and their derivatives but also stimulates the search for methods of synthesising them.

This review deals with studies in recent years of the structural-group compositions of the sulphides, thiophens, and mercaptans in the distillate components of typical petroleums, studies of the chemical reactions and the possible applications of the petroleum OSC discussed, and the existing schemes for the isolation of the OSC from petroleum distillates are analysed.

II. METHODS FOR THE ISOLATION AND DIFFERENTIATION OF ORGANOSULPHUR COMPOUNDS IN PETROLEUM DISTILLATES

Almost all petroleums contain between 0.01 and 10% of sulphur (S_{tot}).[4] Sulphurous ($0.5 < S_{tot} \leq 1.9\%$) and highly sulphurous ($S_{tot} > 1.9\%$) petroleums, whose contribution to the world production is ~60%, are of greatest interest. The OSC content in the petrol (40–200 °C), kerosene (150–250 °C), and gas-oil (190–450 °C) distillates is usually not more than 1.5, 5, and 10 wt.% respectively and the study of the structures and compositions of the OSC requires their preliminary concentration. Petroleum distillates are multicomponent mixtures of isomers of paraffinic, naphthenic, and aromatic hydrocarbons as well as sulphur, nitrogen, and oxygen compounds, for the isolation and separation of which complex multistage schemes involving the application of physical and physicochemical methods of differentiation are used. As physicochemical methods for the analysis and separation of organosulphur compounds have developed and improved, the schemes for their isolation have been modified. Three principal schemes for the extraction of organosulphur compounds from petroleum distillates are known (Fig.1).

The first scheme is based on the application of the adsorption method for the concentration of organosulphur compounds from petroleum distillates. The composition of the organosulphur compounds present mainly in petrol distillates (40–200 °C) has been studied by this scheme[5]. Elution chromatography on silica gel or alumina is usually employed[5-7]. When the adsorption-chromatographic method of concentration is used, the process conditions and the nature of the sorbent and eluents can be varied within wide limits. The sulphur content in the resulting concentrates varies from 5 to 11%; the paraffinic-naphthenic hydrocarbons are then most completely separated, while organosulphur compounds—sulphides, thiophens, and mercaptans—are concentrated together with aromatic hydrocarbons. These concentrates are then subjected to further differentiation by complex formation with mercury acetate[5], low-temperature extraction (HI,[8] H_2SO_4[9]), the formation of adducts with 1,3,5-trinitrobenzene,[8,10] gel permeation chromatography[11–15], fractionation, etc.

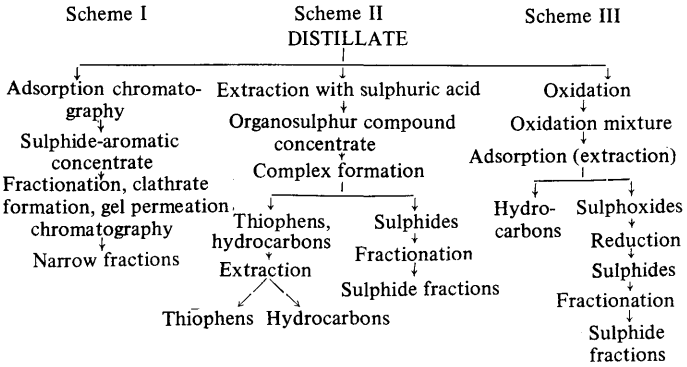


Figure 1. Schemes for the isolation and separation of organosulphur compounds in petroleum distillates.

Selective extraction is used for the preferential removal of sulphides from petroleum fractions (40–360 °C) by scheme II.[16,17] This method makes it possible to isolate from the distillate up to 70% of the sulphides, whose content in the concentrates is ≤60% in sulphuric acid extraction[16] and 40–50% in extraction by organic solvents[17]. Together with sulphides, hydrocarbons and thiophen derivatives are coextracted into the concentrates; the concentrates obtained with the aid of organic solvents are distinguished by an enhanced content of aromatic hydrocarbons. The OSC content in the sulphuric acid concentrates can be raised to 95–97% by means of re-extraction with sulphuric acid[18] or a countercurrent using another solvent[19]. For the selective extraction of sulphides from distillates and sulphuric acid concentrates of OSC, complex formation with silver nitrate is used[20], whereby one can obtain sulphides which are virtually free from thiophens and hydrocarbons. Titanium tetrachloride[21] and aluminium chloride[22] are also used as complex-forming agents; the degree of extraction of sulphur from the distillates is then low (39%), since oxygen and organonitrogen compounds are extracted together with the OSC.

Scheme II has been used[5] to identify the organosulphur compounds in petrol distillates (40–190 °C) and to establish the structural-group composition of organosulphur compounds from the middle distillates (15–360 °C) of a series of petroleums[23–25]. However, this scheme is apparently relatively inapplicable to the fraction of heavy high-tar petroleums owing to the marked charring in the sulphuric acid extraction stage and the low yield of complexes with silver nitrate.

The technology of the preparation of concentrates of organosulphur compounds from middle petroleum distillates on an experimental industrial scale has been developed on the basis of this method[26,27]. The large batches of concentrates of organosulphur petroleum compounds obtained were tested for the first time on an industrial scale in various branches of the national economy[28,29].

Scheme III, proposed[30] for the isolation and investigation of sulphides in petroleum distillates, is based on the chemical method of isolation. The authors[30] developed conditions for the selective oxidation of sulphides in a mixture with thiophens and hydrocarbons. The sulphoxides isolated are either desulphurised or reduced and the composition of the resulting hydrocarbons or sulphides is investigated; it is then possible to characterise up to 80% of the sulphides (relative to their initial content). The method is applicable to the light and middle distillates and has been used successfully for the industrial preparation of sulphoxides[31].

This scheme has been used in the investigation of the sulphides in the Romashki petroleum[32], the accumulated South Uzbekistan petroleum[33], the Khaudag and Kyzyl-Tumshuk petroleums[34], and the organosulphur compounds in the deparaffinated distillate of the Kuwait petroleum[35].

Apart from the adsorption methods for the isolation of mercaptans from petroleum distillates, methods involving extraction with 40% alkali[36], sodium aminoethoxide in anhydrous ethylenediamine[37], and the metal oxides and salts[38] are widely used. The degree of extraction of mercaptans is low (up to 40%) when mercury chloride, mercury acetate, cadmium acetate, and silver nitrate are used[38], about 60% for extraction with an ethanol solution of 40% KOH,[36] 68% for extraction with sodium aminoethoxide[37], and up to 96% for extraction with iron dodecarbonyl[39]. Mercaptans are regenerated from the mercaptides or disulphides obtained by these methods in order to investigate their structural-group composition. After demercaptanisation, the residual OSC in the distillates are isolated in accordance with schemes I and II (Fig.1).

Sometimes the order of treatment can be altered. Thus, in the study of mercaptan-containing distillates, adsorption is carried out initially and then alkaline extraction, etc.[8] It is noteworthy that repeated treatment with reagents is usually necessary. Depending on the aim, fractionation, molecular distillation[8], thermal diffusion separation[40], etc. are used in various stages.

Concentrates of thiophens, sulphides, and mercaptans or narrow fractions are investigated by a set of various physical methods of analysis, including infrared and ultraviolet spectroscopy, ^1H NMR, mass spectrometry, hydrodesulphurisation on Raney nickel, gas–liquid chromatography, chemical reactions, and elemental and functional analyses in order to identify the components and determine the structural-group composition.

III. INVESTIGATION OF THE COMPOSITIONS OF CONCENTRATES OF ORGANOSULPHUR COMPOUNDS IN PETROLEUM DISTILLATES

The study of the composition of the OSC has been developing in three main directions: (1) group analysis of the OSC in petroleums and petroleum products; (2) identification of the OSC, which is characteristic of studies of the OSC in the petrol–ligroin distillates (40–240 °C); (3) determination of the structural-group composition of the OSC, which is most widely used in the study of the kerosene–gas-oil distillates (150–535 °C).

1. The Group Composition of Petroleum OSC

The analysis of the group composition of the OSC in petroleums and distillates involves the determination of elemental (S_S), hydrogen sulphide (S_{H_2S}), mercaptan (S_{merc}), disulphide (S_{RSSR}), and sulphide (S_{sulph}) sulphur. The unidentified component is usually referred to as the residual or thiophen sulphur (S_{res}); it usually constitutes a large fraction, owing to the difficulties arising in the analysis and the study of the composition and structure of the petroleum OSC. The residual sulphur includes (apart from that in thiophens) the sulphur in diaryl and alkyl aryl sulphides, but only a small amount of these compounds has been found in petroleums[13].

Hitherto systematic studies have been made of the group compositions of the OSC present in the distillates (40–300 °C) for the majority of the petroleums in the USSR (250 specimens of petroleums and distillates boiling up to 300 °C),[43] America, and the Near East[4]. These data are necessary for the technological characterisation of sulphurous and highly sulphurous petroleums. However, the existing methods for the analysis of the group composition of the OSC have been developed for the low-boiling and middle distillates and are inapplicable to the high-boiling distillates (above 360 °C), a characteristic feature of which is the similarity and averaging of the properties of the components.

The results of the study of the group composition of the OSC of certain petroleums are presented in Table 1. Depending on the group composition of the OSC contained in the distillates, petroleums can be divided by convention into three types: thiophen petroleums (type I), which contain mainly thiophen sulphur and not more than 10% of sulphide sulphur, while the remaining groups are absent; sulphide petroleums (type II) containing thiophens and sulphides, while the content of mercaptans is not more than 5%; mercaptan petroleums (type III), which contain comparable amounts of sulphides, thiophens, and mercaptans and there is also a possibility of the presence of disulphides, hydrogen sulphide, and elemental sulphur (see Table 1). Since the content of hydrogen sulphide in petroleum is variable and depends on the sampling, storage, and transport conditions, its amount in petroleum is usually not determined. Petroleums of the first and third types are encountered in nature much more rarely than those of the second type.

Table 1. The group compositions of the organosulphur compounds in certain world petroleums (relative content, %).

Petroleum	Refs.	S_{tot}	S_{res}	S_{sulph}	S_{merc}	S_{RSSR}	S_S
Type I							
Usinsk, USSR	[41]	2.07	100	0.00	0.00	0.0	0.00
Yaregsk, USSR	[42]	1.11	100	0.00	0.00	0.0	0.00
Ust'-Balyk, USSR	[43]	1.45	89.0	11.0	0.00	0.0	0 00
Type II							
Santa Maria, California	[4]	4.99	58.20	41.6	0.20	0.0	0.00
Wester Surgut, USSR	[44]	3.00	68.5	31.5	0.00	0.0	0.00
Arlansk, USSR	[45]	1.02	70.0	30.0	0.00	0.0	0.00
	[23]	3.05	76.17	23.6	0.23	0.0	0.00
Type III							
Terekli, USSR	[43]	2.27	81.8	8.8	9.07	0.0	0.29
Orenburg, USSR	[46]	2.33	84.5	7.2	8.30	0.0	0.00
Wasson, Texas	[4]	1.85	52.5	24.6	15.3	7.4	0.10
Deep River, Michigan	[4]	0.58	28.6	3.0	45.9	22.5	0.01

Each of the above types of petroleum is not characterised solely in terms of differences between their group compositions. The thermal stability of the petroleum OSC is an important technological characteristic[43], decreasing on passing from petroleums of type I to those of type III, which must be taken into account in the study of the composition and structure of the OSC. The content of sulphur in all the consecutively boiling fractions of petroleums of types I and II is higher the higher its content in the petroleum. The sulphur content in the low-boiling distillates of petroleums of type III can be higher than in the high-boiling distillates and depends mainly on the thermal stability of the OSC. The group compositions of straight-run distillates (particularly petrol distillates) of petroleums of various types therefore differ greatly (Table 2). With increase of the boiling point of the distillate, the difference is smoothed out.

Table 2. The proportions of organosulphur compounds in the distillates of certain petroleums.

Sulphur	Boiling range of distillate, °C		
	40–200	200–360	360–410
Type I (Usinsk) (Ref.41)			
Overall, wt.% of distillate (*A*)	0.06	0.93	1.15
Overall, % of total sulphur in petroleum (*B*)	0.2	9.5	4.5
Sulphide, % of total sulphur in distillate (*C*)	25	—	—
Thiophen, % of total sulphur in distillate (*D*)	75	100	100
Type II (Western Surgutsk) (Ref.44)			
A	0.16	2.0	3.0
B	0.83	23.2	9.2
C	96	60	47
D	4	40	53
Type III (Orenburg) (Ref.46)			
A	0.53	1.1	1.7
B	10.9	30.0	13.6
*E**	52.0	16.0	6.0
C	39.0	24.0	12.5
D	9.0	60.0	81.5
Type III (Markovsk) (Ref.43)			
A	0.96	0.73	—
B	29.9	16.1	

*Mercaptan sulphur, % of total sulphur in distillate.

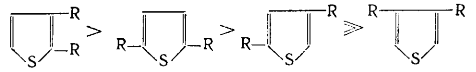
It is noteworthy that active sulphur compounds (S, H_2S, RSH, RSSR) are mainly concentrated in the low-boiling distillates.

2. Identification of Petroleum OSC

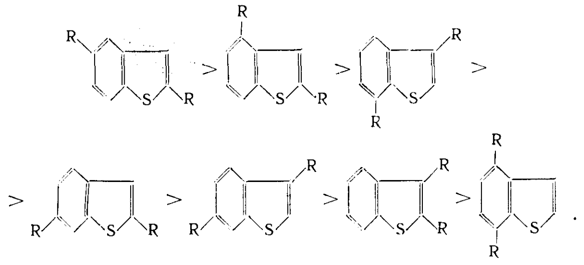
The identification of the OSC in petroleum distillates is a fairly complex problem, as a result of which only 200 organosulphur compounds have been identified in the course of 90 years[5,8]. The results of the identification permit the conclusion that, in the petrol distillates (40–200 °C) of type I petroleums, the OSC consist of alkylthiophens and their derivatives, those in type II petroleums are mainly cyclic sulphides, and those in type III petroleums are aliphatic and cyclic mercaptans and sulphides. All the potential isomers of the sulphides and mercaptans, ranging from C_3 to C_7 (with the exception of unstable compounds containing less than 4 carbon atoms in the ring), are present in these distillates of petroleums of the first and second types. The majority of monocyclic sulphides in petroleums consist of alkylthiacyclopentanes and alkylthiacyclohexanes, the amount of the latter being smaller by a factor of ~2 (which follows from the analysis of the literature data[47–50]). *gem*-Substituted, α,β-disubstituted (in five- and six-membered sulphides), and α,β,γ-trisubstituted (in six-membered sulphides) are more rarely encountered among cyclic sulphides.

The main bulk of the branched aliphatic sulphides and mercaptans as well as paraffins isolated from the distillates consist of isomers with a single branch in the hydrocarbon group[47,48]. Compounds with groups located in the α- and β-positions relative to the sulphur atom are usually encountered. The number of isomers with two branches in the group is much smaller and those with three and more branches have not so far been detected[47–51].

Among the identified C_4–C_7 alkylthiophens[50,51] and C_8–C_{11} benzothiophens[7,8,52–57], the α-derivatives are usually encountered, the isomers of the disubstituted thiophens forming the following sequence in terms of their relative contents in petroleum:



while disubstituted benzothiophens give rise to the sequence



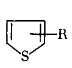
Eighteen C_8–C_{11} alkylthiaindans, mainly with methyl and ethyl substituents, have been identified. The substituents are usually located in the 2- and 3-positions relative to the sulphur atom[6].

Identification made it possible to characterise the OSC in the low-boiling petroleum distillates and to deduce the most likely structures of the compounds in the high-boiling distillates. However, one should note that it is at present impossible to carry out an exhaustive identification of the OSC in the kerosene–gas-oil distillates (150–450 °C). Qualitative identification of certain successfully isolated components from the distillates does not allow inferences about the composition and properties of the mixture of OSC in the concentrates. Therefore the study of the quantitative structural-group composition of the OSC is the most valuable procedure and the only one available procedure for kerosene–gas-oil distillates.

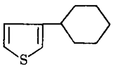
3. The Structural-Group Composition of the Petroleum OSC

The structural-group composition of the OSC has been determined for the 150–250°, 190–360°, 360–450°, and 370 to 535 °C distillates of various petroleums of the USSR,[23,41–46] America, and the Near East.[8,11–15] The majority of the petroleums investigated belong to the second type, whose OSC consist mainly of sulphides and thiophens.

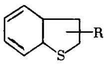
(a) The structural-group composition of the OSC of the distillates of type I petroleums. The typical structures of the OSC found in petroleums of this type are given below:



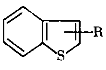
(I)



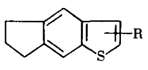
(II)



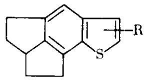
(III)



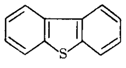
(IV)



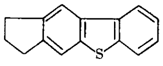
(V)



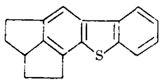
(VI)



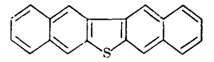
(VII)



(VIII)



(IX)



(X)

Table 3. The structural-group composition of the OSC in the high-boiling distillates of type I petroleums (relative content, %).

Type of structure	Yaregsk (Ref.42), 280-400°	Usinsk (Ref.41), 200-410°	Recluse (Ref.8)*, 370-535°	Swan Hills (Ref.8)*, 370-535°
(I)	6.4	7.0	—	—
(II)	—	0.6	—	—
(III)	5.9	12.8	—	—
(IV)	24.4	23.1	14.4**	18.6**
(V)	16.2	10.7	21.1	12.3
(VI)	10.2	9.9	—	6.1
(VII)	15.4	17.7	6.7	5.2
(VIII)	20.6	9.1	10.0	12.3
(IX)	0.5	7.4	7.8	4.9
(X)	0.4	1.7	6.7	2.3

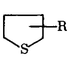
*The sum of the high-molecular-weight thiophens is 33.3 and 38.3% for the Recluse and Swan Hills petroleums respectively.
**Calculated from the data of Rall et al.[8]

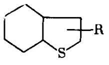
Table 3 shows that the structural-group compositions of the OSC of the 200–410 °C distillates of type I petroleums are fairly close[41,42]. Alkylbenzothiophens (IV) constitute one-fourth of the OSC. Cycloalkano- and bicycloalkano-derivatives of benzothiophens [(V) and (VI)] and dibenzothiophens [(VIII) and (IX)] constitute an appreciable fraction. Thus the content of the tricyclic and polycyclic structures (V)–(X) in these distillates is 55–65%. The contents of dibenzothiophens (VII) and their derivatives (VIII)–(X) are particularly high in the heavy Yareg petroleum[42]. A low content of alkylthiophens (I) (4–6%) and thiaindans (III) (8–10%) is characteristic of petroleums of type I.

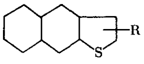
The distillates of type I petroleums do not contain compounds with the sulphide structure probably owing to the catalytic transformations of the petroleum OSC under the influence of the petroleum-bearing rocks and the increased radioactivity of petroleum waters[42].

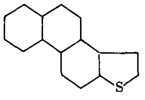
The content of thiophen structures increases with increasing boiling point of the distillate, the quantitative content of benzothiophens, dibenzothiophens, and cycloalkanodibenzothiophens increasing faster than that of alkylthiophens and cycloalkano- and bicycloalkano-benzothiophens. These data, characterised by an increased content of aromatic OSC, agree with the hydrocarbon composition of the distillates, which are distinguished by a higher content of naphthalene and phenanthrene hydrocarbons.

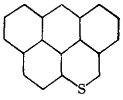
(b) The structural group composition of the OSC in the distillates of type II petroleums. The typical structures of the sulphides detected in these petroleums are as follows:

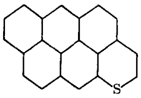

(XI)

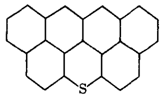

(XII)


(XIII)

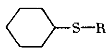

(XIV)

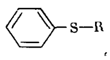

(XV)


(XVI)


(XVII)

$R-S-R'$
(XVIII)


(XIX)


(XX)

With increase of the boiling points of the distillates, the content of sulphides in the OSC diminishes (Table 2). The sulphide component of the OSC in the petrol distillates (40–190 °C) of the Weatern Surgut petroleum consists of almost 90% of thiacycloalkanes. The fraction of thiamonocycloalkanes (XI) is 80%, while the content of thiabicycloalkanes (XII), thiaindans (III), and dialkyl sulphides (XVIII) does not exceed 5–7%.[58]

Thiamonocycloalkanes also predominate (45–55%) in the diesel distillate (190–360 °C) of this petroleum, but their relative content is smaller by ~20–30% than in the petrol distillate. The number of rings in the thiacycloalkane molecules in this distillate increases to 4–5. The content of dialkyl sulphides is reduced by a factor of ~2, while the content of thiaindans remains unchanged[44].

Thiamonocycloalkanes predominate in the 360–410 °C distillate, while the content of thiabicycloalkanes is fairly high[59]; the latter predominate in the 410–450 °C distillate[60]. These data show that the number of rings in the OSC molecules increases with increasing boiling point of the distillate.

Thus the relative content of thiamonocycloalkanes and dialkylsulphides falls on going from a low-boiling to a high-boiling distillate, the content of thiaindans changes little, and that of thiapolycycloalkanes increases.

The absolute content of all types of sulphides in the distillate as a rule increases with increase of the boiling point (Fig.2).[61] The absolute content of thiamonocycloalkanes is a maximum in the 360–410 °C distillate and that of acyclic sulphides is a maximum in the 190–360 °C distillate. The curve representing the proportions of thiamonocycloalkanes as a function of the boiling point of the distillate has a lower slope than the corresponding curves for thiabi-, thiatri-, thiatetra-cycloalkanes, which means that the increase in the number of rings in the molecules of the organosulphur compounds is faster than the increase in the size of the molecules with increase of the length of the alkyl group in the alkylcycloalkane.

Polynuclear OSC with a long side chain or with a naphthene ring as substituents have not been discovered in the 190° to 360 °C distillates. This may be evidence that the increase in molecular weight is to a large extent associated with the increase of the degree of substitution.

In contrast to sulphides, the content of thiophens increases and becomes dominant in the high-boiling distillates. For example, alkylthiophens (100%), constituting 2–4% of the total content of the OSC, have been found in the petrol distillate (40–200 °C) of the Western Surgut petroleum. The dominant structural group in the thiophen component of the 190–360 °C distillate[44] is alkylbenzothiophens (60–80%), while alkylthiophens constitute not more than 5–7%. The thiophen components of the 360–410° and 410–450 °C distillates[59,60] contain mainly alkylbenzothiophens (~40%) and cycloalkanobenzothiophens (16%). The absolute content of alkylthiophens is a maximum in the 360–410 °C distillate: on passing to the high-boiling distillate, the content of cycloalkanobenzothiophens and dibenzothiophens increases most sharply; the amount of the remaining structural groups of thiophens increases uniformly (Fig.3).[61]

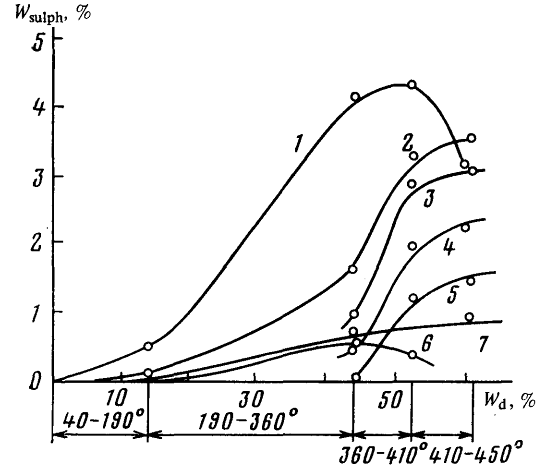


Figure 2. The proportions of thiamonocycloalkanes (curve *1*), thiabicycloalkanes (curve *2*), thiatricycloalkanes (curve *3*), thiatetracycloalkanes (curve *4*), thiapentacycloalkanes (curve *5*), dialkyl sulphides (curve *6*), and thiaindans (curve *7*) in the 40–190°, 190–360°, 360–410°, and 410–450° distillates of the Western Surgut petroleum (W_d = yield of distillate, wt.% of petroleum; W_{sulph} = content of sulphides, wt.% of the corresponding distillate).

The quantitative contents of the structural groups of sulphides and thiophens in the high-boiling distillates of various type II petroleums are compared in Table 4. It is noteworthy that the compositions of thiacycloalkanes are similar, the differences between the relative contents of alkylthiabi-, alkylthiatri-, and alkylthiatetra-cycloalkanes being particularly small. The increased content of thiamonocycloalkanes and the reduced content of thiapolycycloalkanes in the Wester Surgut petroleum, compared with the other petroleums quoted, is consistent with the differences between the boiling points of their distillates. Compared with the sulphide component of the OSC, the structural-group compositions of the thiophen components of these petroleums differ to a greater extent.

The results of the estimates of the overall contents of the individual structural groups in straight-run distillates (40–450 °C) are presented in Fig.4. Evidently the structural groups present in greatest amounts comprise alkylbenzothiophens and thiamono-, thiabi-, and thiatri-cycloalkanes; the sum of the acyclic sulphides is 5%.[61] The relative content of compounds with increasing numbers of rings in their molecules diminishes uniformly for thiacycloalkanes and non-uniformly for thiophens. The diagram shows that the content of alkylbenzothiophens greatly exceeds that of all the remaining thiophen groups. This can apparently be accounted for by the higher stability of alkylbenzothiophens and the possibility of the presence of a large amount of isomers. Some of the alkylbenzothiophens are probably the products of the thermal degradation of the more condensed thiophen-containing polynuclear structures.

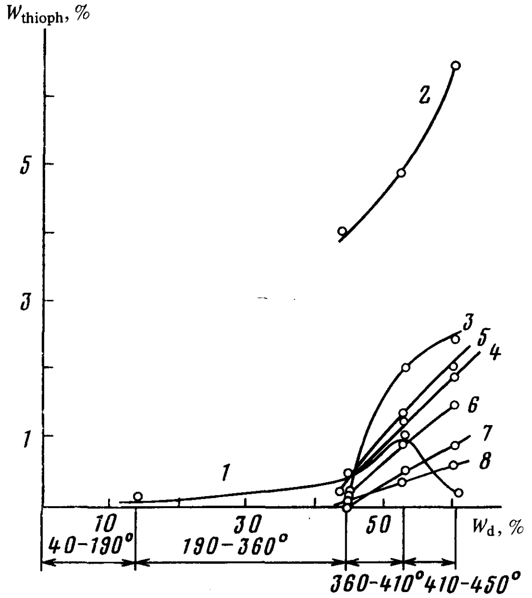


Figure 3. The proportions of alkylthiophens (curve *1*), alkylbenzothiophens (curve *2*), alkylcycloalkanobenzothiophens (curve *3*), bicycloalkanobenzothiophens (curve *4*), dibenzothiophens (curve *5*), cycloalkanodibenzothiophens (curve *6*), thienophenanthrenes (curve *7*), and dicycloalkanothienophenanthrenes (curve *8*) in the 40–190°, 190° to 360°, 360–410°, and 410–450° distillates of the Western Surgut petroleum (W_d = yield of distillate, wt.% of petroleum; W_{thioph} = content of thiophens, wt.% of the corresponding distillate).

Table 4. The content (wt.% of petroleum) of the principal structural groups of thiophens and thiacycloalkanes in 370–535 °C high-boiling distillates of type II petroleums.

Type of structure	Prudhoe Bay*	Gach-saran*	Wilmington*	Western Surgut** (Ref.57)
(I)	—	—	0.017	0.015
(II)	—	—	0.027	0.015
(IV)	0.18	0.33	0.20	0.50
(V)	0.10	0.24	0.17	0.19
(VI)	0.07	0.17	0.13	0.15
(VII)	0.26	0.35	0.31	0.16
A***	0.59	0.47	0.63	0.18
(XI)	0.052	0.245	0.193	0.23
(XII)	0.150	0.269	0.272	0.26
(XIII)	0.190	0.262	0.286	0.23
(XIV)	0.160	0.250	0.202	0.17
(XV)	0.119	0.256	0.207	0.06
(XVI)	0.065	0.193	0.195	0.05
(XVII)	0.050	0.250	0.185	—

*Calculated from the data of Rall et al.[8]

**410–450 °C distillate.

***A = sum of high-molecular-weight thiophens.

(c) The structural-group composition of the OSC of type III petroleums. A considerable amount of OSC (S_{tot} = 0.53) has been found in the low-boiling distillates of petroleums of this type, exceeding by an order of magnitude that in the analogous distillates of type I and II petroleums.

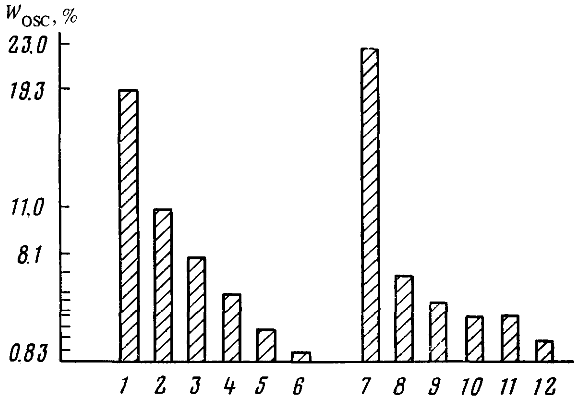


Figure 4. The proportions (% of total OSC) of thiamonocycloalkanes (column *1*), thiabicycloalkanes (column *2*), thiatricycloalkanes (column *3*), thiatetracycloalkanes (column *4*), thiapentacycloalkanes (column *5*), thiahexacycloalkanes (column *6*), alkylbenzothiophens (column *7*), cycloalkanobenzothiophens (column *8*), bicycloalkanobenzothiophens (column *9*), thiaindans (column *10*), dibenzothiophens (column *11*), and alkylthiophens (column *12*) in the 40° to 450 °C distillates of the Western Surgut petroleum.

With increase of the boiling point of the distillate, the content of mercaptans and sulphides falls, while that of thiophens increases (Table 2). The content of mercaptans decreases more than that of the sulphides. The absolute content of mercaptans is a maximum in the 200–360 °C distillate. The mercaptans in the low-boiling distillates are mainly primary or secondary. The 200–360 °C distillate contains a very large amount of cyclic mercaptans[62].

The sulphides consist mainly of thiamonocycloalkanes and acyclic sulphides (Fig.5). It is noteworthy that, in contrast to the corresponding distillates of type II petroleums, these distillates contain a considerable amount of dialkyl sulphides and alkyl cycloalkyl sulphides[46]. Among thiophens, dibenzothiophens predominate, particularly in the 200–360 and 360–410 °C distillates. The content of alkylthiophens is slight[62]. The curves illustrating the relative contents of dibenzothiophens as well as cycloalkano- and bicycloalkanobenzothiophens in the distillates become steeper with increase of the boiling points of the latter than the corresponding curves for benzothiophen and particularly alkylthiophen derivatives. These results show that the amount of condensed OSC molecules increases sharply with increase of the boiling point of the distillate. Thus type III petroleums are similar to type I petroleums in terms of the structural-group composition of the thiophens and the nature of their distribution among the distillates and can serve as the starting material for the preparation of benzo- and dibenzo-thiophens.

4. Certain Generalisation Concerning the Individual and Structural-Group Compositions of the OSC of World Petroleums

On the basis of the results of the identification [of components] and the study of the structural group-composition of the OSC of the petrol, kerosene, and gas-oil distillates, it is possible to make certain comparisons and generalisations. The principal components of the 40–535 °C distillates are benzo- and dibenzo-thiophens in petroleums of the thiophen type, thiacycloalkanes and benzothiophens in petroleums of the sulphide type, and dibenzothiophens, thiacycloalkanes, acyclic sulphides, and mercaptans in petroleums of the mercaptan type.

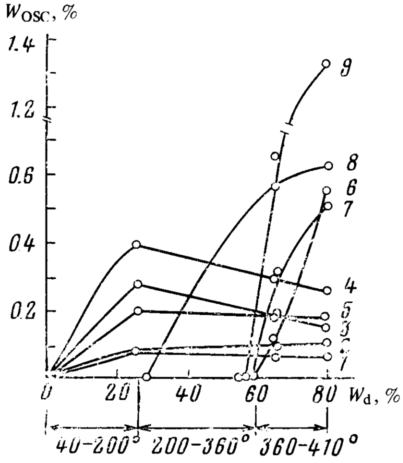


Figure 5. The proportions of alkyl cycloalkyl sulphides (curve *1*), thiaindans (curve *2*), dialkyl sulphides (curve *3*), thiamonocycloalkanes (curve *4*), alkylthiophens (curve *5*), cycloalkanobenzothiophens (curve *6*), bicycloalkanobenzothiophens (curve *7*), benzothiophens (curve *8*), and dibenzothiophens (curve *9*) in the 40–200°, 200–360°, and 360° to 410 °C distillates of the Orenburg petroleum (W_d = yield of distillate, wt.% of petroleum; W_{OSC} = OSC content, wt.% of the corresponding distillate).

The thiacycloalkanes consist mainly of five- and six-membered isomers. The number of rings increases with increasing boiling point of the fraction. The maximum content of isomers with the greatest number of substituents is characteristic of thiamonocycloalkanes, the substituents being linked to different carbon atoms. The kerosene distillate (150–250 °C) contains 25% of α,α′-dialkylthiamonocycloalkanes with substituents having the straight-chain structure only, while the diesel distillate (190–360 °C) contains ~5% of similar structures relative to the total amount of thiamonocycloalkanes[23].

A detailed comparison of the structural-group compositions of the sulphides isolated from diesel distillates (190–360 °C) with petroleums of the sulphide type shows that they are qualitatively similar (Table 5). The quantitative contents of the individual structural groups in the distillates of highly sulphurous petroleums (for example the Arlansk and Western Surgut petroleums) are approximately the same; the corresponding structural groups are present in a smaller amount in the distillates of sulphurous petroleums (the Samotlor petroleum). However, the relative contents of analogous structures are fairly similar in distillates of petroleums of the same type. Thus the contents of the principal components (thiamono- and thiabi-cycloalkanes) differ by not more than 15–20%. This result is important for the practical utilisation of petroleum sulphides.

Table 5. The structural-group composition of the sulphides in the 190–360 °C distillates of type II petroleums (relative content, %).

Type of structure	Petroleum					
	Arlansk (Ref.23)	Western Surgut (Ref.44)	Samotlor (Ref.45)	South Uzbek (Ref.33)*	Khaudag (Ref.34)*	Kyzyl-Tumshuk (Ref.34)*
(III)	4.71	3.30	3.20	6.4	3.6	2.8
(XI)	45.58	56.0	57.58	59.4	59.2	53.0
(XII)	20.99	16.6	20.96	19.7	25.0	24.0
(XIII)	12.66	13.0	8.54	8.7	10.4	9.4
(XIV)	4.71	5.40	2.44	1.9	1.3	3.6
(XVIII)	6.94	3.1	3.66	1.7	0.5	4.7
(XIX)	2.99	3.2	3.12	2.2	—	2.5
(XX)	1.42	—	0.50	—	—	—

*Calculated from data in Refs.33 and 34.

Comparison of the quantitative contents of the individual structural groups of thiophens in different petroleums revealed certain characteristic features. Benzothiophens predominate in the distillates of highly sulphurous type II petroleums[9]. Both thiophens and benzothiophens and naphthenobenzothiophens have been found in approximately equal amounts in the distillates of sulphurous petroleums of this type[45]. Condensed derivatives of benzo- and dibenzothiophens greatly predominate in the distillates of type I and III petroleums.

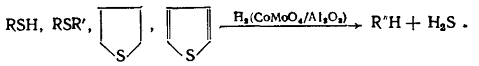
It follows from the data presented above that the relative contents of the individual and structural groups of OSC within the limits of each class (sulphides, thiophens, benzothiophens, and naphthenobenzothiophens) are approximately of the same order of magnitude for different petroleums, as in the case of hydrocarbons[63]; the contents of each class of compounds in different petroleums are different.

The data presented permit the conclusion that certain petroleum distillates can serve as a realistic source of natural mercaptans, thiacycloalkanes, benzothiophens, dibenzothiophens, etc.

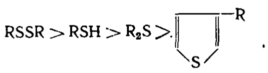
IV. CHEMICAL PROPERTIES OF THE MERCAPTANS, SULPHIDES, AND THIOPHENS IN PETROLEUM

The petroleum OSC consist of a mixture of isotypical structures of different molecular weights, the functionality of the molecules decreasing as a rule with increasing molecular weight. One can therefore postulate that only those reactions which exhibit a low selectivity within the homologous series and are at the same time highly sensitive to the functional characteristics of the molecules can be used successfully in the chemistry of petroleum OSC. This is why only a few of the known reactions of individual mercaptans, sulphides, and thiophens have been applied to petroleum systems.

The reaction most thoroughly investigated in this sense is that of hydrogenolysis—one of the most effective methods for the desulphurisation of all the groups of OSC:



The catalysts for the hydrodesulphurisation of the OSC are cobalt, molybdenum, tungsten, nickel, and iron oxides or sulphides or their mixtures on alumina. The process is carried out under a hydrogen pressure from 4 to 70 atm at 300–425 °C (depending on the composition of the OSC and their content in the petroleum products)[64]. In terms of their capacity to undergo hydrodesulphurisation, the OSC can be arranged in the sequence



Depending on the conditions, the process can be carried out with a quantitative conversion of the OSC. More severe conditions are required in the hydrodesulphurisation of compounds with a high molecular weight and a large number of rings in their molecules and with a high degree of condensation. Hydrogenolysis has been widely used in industrial large-scale processes involving the removal of sulphur from petroleum products and also in analytical practice.

The reactions characteristic of specific groups of OSC are examined below.

1. Reactions of Petroleum Mercaptans

Mercaptans are the most reactive compounds among the OSC; they exhibit acidic properties and react fairly readily with alkalies:

$$\mathrm{RSH + NaOH \rightleftarrows RSNa + H_2O} \quad .$$

The reaction is reversible and mercaptans can be regenerated by hydrolysis and for this reason the degree of conversion is low even for low-boiling mercaptans. Aliphatic mercaptans react more readily the shorter their hydrocarbon chain and the lower the degree of branching of the latter. The addition of the so-called "solutisers" increases the degree of conversion. The solutisers tested have included *m*- and *p*-cresols, phenol, ethanol, and methanol[65,66]. The use of the latter makes it possible to achieve a virtually theoretical conversion of mercaptans (90–95%). However, after regeneration the yield of mercaptans does not exceed 60%,[66] because they are readily oxidised by atmospheric oxygen to disulphides. A high degree of extraction of petroleum mercaptans (40–60%) is observed when they are treated with a KOH solution containing monoethanolamine[36]. The subsequent oxidation of the resulting mercaptans to disulphides takes place in the presence of catalysts—copper(I) chloride or the sodium salt of cobalt-disulphophthalocyanine ($C_{32}H_{14}O_6N_8S_2CoNa_2$):

$$\mathrm{RSNa + O_2 + H_2O \xrightarrow{cat} RSSR + NaOH} \quad .$$

The method makes it possible to remove mercaptan sulphur almost completely from petrols[66], light hydrocarbon fractions, and gas condensates[67].

Disulphides can be formed in acetic acid solution in the presence of lead tetra-acetate[3] and in concentrated sulphuric acid. Mercaptans are capable of substituting the carbonyl groups in iron carbonyl complexes[68]:

$$\mathrm{Fe_3(CO)_{12};\ Fe_2(CO)_9;\ Fe(CO)_5} \ .$$

The relative reactivities of the OSC form the sequence (in proportions of 14 : 9 : 1)

$$\mathrm{RSH > RSSR > RSR} \ .$$

Mercaptans react most fully with iron dodecarbonyl, forming iron tricarbonyl mercaptides. When dry hydrogen chloride is passed through iron tricarbonyl mercaptides in solution in dodecane at elevated temperatures, the corresponding mercaptans are formed. Treatment of this solution with copper(II) chloride makes it possible to obtain the disulphides. Oxidation with concentrated nitric acid leads to a quantitative yield of the corresponding alkanesulphonic acid (isolated as the sodium salt)[68]. The sodium salts of sulphonic acids can be obtained by the oxidative chlorination of petroleum mercaptans followed by hydrolysis with alkali[69].

Petroleum mercaptans react with heavy metal oxides and salts. The reactions with silver nitrate[38], cadmium acetate and chloride[65], and mercury acetate[66] have been investigated; in all cases the degree of conversion of the mercaptans is low (~60–70%). In the reaction with mercury acetate the tertiary mercaptans decompose with dissociation of the C–S bond. The reaction with sodium aminoethoxide in anhydrous ethylenediamine is less sensitive to the structural features of mercaptans[37]:

$$\mathrm{RSH + H_2NC_2H_4ONa \rightarrow RSNa + H_2NC_2H_4OH} \quad .$$

The degree of conversion of the mercaptans is almost quantitative.

Bis-sulphides have been obtained by the reaction of petroleum mercaptans with 1,2-dibromoethane:

$$\mathrm{RSNa + BrCH_2{-}CH_2Br \rightarrow RSCH_2{-}CH_2SR + NaBr} \quad .$$

The reaction proceeds in an alcoholic solution of alkali and the yield of bis-sulphides is 75–85%,[70] the products being effective stabilisers in the thermo-oxidative degradation of poly(methyl methacrylate).

Petroleum mercaptans constitute a readily available starting material for the synthesis of vinyl sulphides[71];

$$\mathrm{RSH + CH \equiv CH \xrightarrow{KOH(10-20\%),\ 70-140^\circ} RS{-}CH{=}CH_2} \ .$$

The reaction is quantitative and the products can be used as insecticides, flotation agents, and as a base for varnishes. The condensation of mercaptans in the petrol and kerosene distillates with ethylene chlorohydrin followed by oxidation and dehydration makes it possible to obtain alkyl vinyl sulphones, which are effective herbicides[72]:

$$\mathrm{RSH \rightarrow RS{-}CH_2{-}CH_2{-}OH \rightarrow RSO_2CH_2CH_2OH \rightarrow RSO_2CH{=}CH_2} \ .$$

Petroleum mercaptans react fairly completely with olefins[73,74]:

$$\mathrm{R{-}S{-}H + H_2C{=}CHR \rightleftarrows R{-}S{-}CH_2{-}CH_2{-}R} \quad .$$

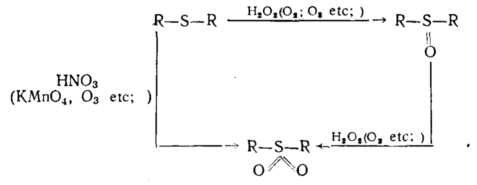
The C–C bonds in olefins were thi-ylated with the mercaptans of the low-boiling fraction (40–200 °C) of the Orenburg petroleum containing 0.22 wt.% of mercaptan sulphur and 0.25 wt.% of sulphide sulphur[62]. The catalysts used were benzoyl peroxide, aluminium chloride, ethylenealuminium dichloride, and an aluminium-containing catalytic complex. The results indicate a fairly high degree of conversion of the petroleum mercaptans (70–80%). Among the olefins investigated, best results were obtained for 2-methylpent-1-ene, containing an active carbonium ion attached to the double bond, and the best catalysts were ethylenealuminium dichloride and the active aluminium-containing complex. Analysis of the group composition of the product agreed satisfactorily with the results of the physicochemical study of the sulphide concentrate isolated from this fraction by extraction with sulphuric acid. Comparison of the structural-group compositions of the sulphides present in the petrol distillate and obtained from the petroleum mercaptans shows that the main bulk of the former sulphides have a lower molecular weight than those obtained from the mercaptans[62].

A lower degree of conversion is characteristic of the interaction with olefins of the mercaptan concentrate obtained from the higher-boiling distillate (200–360 °C) in which the content of mercaptan sulphur is 8.25%.[62] This can apparently be accounted for by the lower thi-ylating activity of cyclic mercaptans, ~30% of which were detected in the given concentrate relative to the total OSC content. Among the olefins tested, low-molecular-weight olefins, namely isoprene and 2-methylpent-1-ene, proved to be the most reactive in the reaction with mercaptans[62,74]. Investigations have shown that aliphatic mercaptans can be converted almost quantitatively into sulphides, which can be more conveniently isolated and their structural-group composition investigated, because, as shown above, mercaptans are oxidised during isolation and intense corrosion of the detector is observed in analysis by gas–liquid chromatography (GLC).

The possibility of the catalytic conversion of petroleum mercaptans into sulphides makes it possible to regard mercaptan-containing petroleums and gas condensates as additional sources of raw materials for the preparation of sulphides.

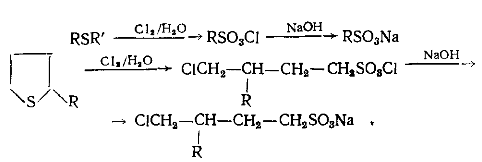
2. Reactions of Petroleum Sulphides

Reactions involving the oxidation of petroleum sulphides to sulphoxides and sulphones have been vigorously investigated in the last 10–15 years:

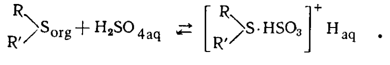


The oxidants used in these reactions are hydrogen peroxide[2,75], atmospheric oxygen in the presence of transition metals and their oxides and sulphides[76], heteropolyacids[77], organic hydroperoxides, etc. The highest selectivity and highest degree of conversion are attained when the reaction is carried out at 70–80 °C in the presence of catalytic amounts of H_2SO_4. The yield of sulphoxides is 70–80%.[2] Depending on the conditions, the oxidation can be continued until the formation of sulphones in 90–100% yields. Sulphides with a higher molecular weight are oxidised under more severe conditions. This reaction is very important for the preparation of substances with biological activity[78] and complex-forming capacity[79], i.e. substances with more valuable properties than the initial petroleum sulphides.

Different fractions of sulphides isolated from distillates of highly sulphurous petroleums readily undergo oxidative chlorination. Subsequent hydrolysis of the reaction products yields the sodium salts of sulphonic acids[80]:



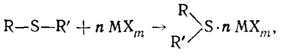
Sulphuric acid has been used for a long time for the removal of OSC from petroleum products. It has been established that the interaction of petroleum sulphides with sulphuric acid is exothermic[18,81] and results in the formation of a protonated complex:


$$\begin{matrix}R\\R'\end{matrix}\!\!>S_{org}+H_2SO_{4aq}\rightleftarrows\left[\begin{matrix}R\\R'\end{matrix}\!\!>S\cdot HSO_3\right]^+H_{aq}\ .$$

The degree of protonation depends on the molecular weight and structure of the sulphide, the sulphuric acid concentration, and the extraction temperature. With increase of the molecular weight of the sulphide, protonation takes place at a lower temperature and with more concentrated acid[9,82].

Apart from sulphuric acid, HI,[83] HF,[55] and copper sulphate dihydrochloride[84] have been tested as protonating agents; the first two reagents have not found extensive application owing to the occurrence of side reactions (the dissociation of the C–S bond in sulphides with a tertiary carbon atom in the α-position relative to the sulphur atom, coextraction of aromatic hydrocarbons, and the predominance of the reaction with aromatic hydrocarbons) and the difficulty of regenerating the extracted sulphides. Copper sulphate dihydrochloride is a milder protonating agent, which is active in reactions with low-molecular-weight sulphides.

Petroleum sulphides undergo fairly readily addition reactions with heavy metal salts:

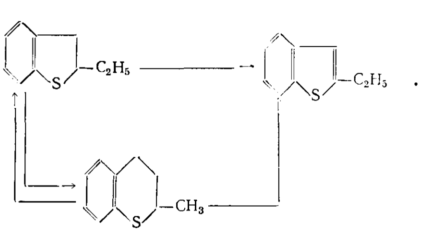

$$R{-}S{-}R'+n\,MX_m\rightarrow\begin{matrix}R\\R'\end{matrix}\!\!>S\cdot n\,MX_m,$$

$M = Ag^+, Hg^{2+}, Al^{3+}, Ti^{4+}, Sn^{4+};$

$X = Cl^-, Br^-, CH_3COO^-, NO_3^-$.

It has been established that, with increase of molecular weight and with decrease of the symmetry of the sulphides, their reactivity falls[85]. Mercury derivatives have therefore been obtained mainly for the sulphides in the petrol–ligroin distillates[5]. Titanium[86] and aluminium[87] salts proved to be less selective complex-forming agents, since they react vigorously also with other hetero-organic compounds containing nitrogen and oxygen.

The catalytic dehydrogenation and isomerisation of thiaheterocycloalkanes of different structure are promising reactions:

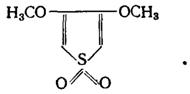


It has been shown[88] that the reaction proceeds via an ionic mechanism involving the successive elimination of a hydride ion and a proton. It has been found that the reactions are effective in the presence of quinoline-treated ASK-Na or ASK catalysts.

3. The Reactions of Petroleum Thiophens

Despite the considerable content of thiophens of different structure in petroleums, their compositions and properties have been less thoroughly investigated than those of sulphides and mercaptans. This is probably due to the difficulty of isolating them from a mixture with aromatic hydrocarbons and other sulphur compounds and the fact that their main bulk is present in the relatively little studied high-boiling petroleum distillates.

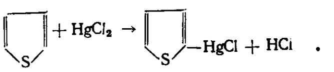
Thiophens are more resistant to oxidation than sulphides. The introduction of electron-donating substituents into the thiophen molecule promotes its oxidation to the sulphone[89]. Stable sulphones are formed in the presence of two symmetrically located substituents:



On treatment with strong oxidants, the side chains are converted into carboxy-groups. As regards the degree of oxidation of petroleum thiophens, the available literature data do not permit a clear-cut analysis, because the oxidised products have been characterised only by their molecular weights and boiling points and the sulphones derived from petroleum thiophens have not been isolated[3,90,91].

Electrophilic substitution reactions are characteristic of thiophens, which is associated with the enhanced electron density in the α-position due to the presence of the sulphur atom. The sulphonation method has been used[92] for the isolation of a mixture of thiophens from petroleum distillates; the degree of their extraction did not exceed 45%.

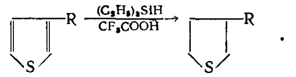
In reactions with bivalent mercury salts thiophens form organometallic derivatives:



However, the regeneration of thiophens from the mercurated products involves considerable losses[93]. The reaction has not therefore found extensive practical applications.

In a series of analytical studies[94–96] of middle and high-boiling distillates the method involving the dealkylation of thiophens free from other groups of OSC was used. It may be that the dealkylation reaction will be of practical importance for the analysis of fairly thoroughly purified concentrates of petroleum thiophens.

Ionic hydrogenation[97] with trifluoroacetic acid and triethylsilane can be used successfully to convert petroleum thiophens into the corresponding sulphides[97]:



The results of experiments on the hydrogenation of thiophen concentrates of different composition have shown that more severe conditions (a longer reaction time and a greater excess of trifluoroacetic acid) are required to attain a 70–86% degree of conversion of a mixture of thiophens than in the hydrogenation of individual thiophens[98]. The study of the structural-group composition of the products showed that the main compounds are monothiacycloalkanes and thiaindans; apparently derivatives of thiophens and benzothiophens were hydrogenated and in the case of the latter only the thiophen ring was hydrogenated.

Sulphuric acid concentrates of OSC obtained after the ionic hydrogenation reaction contain up to 70% of thiacycloalkanes and 20% of thiaindans, the overall sulphide content being 96%. Thus the application of the ionic hydrogenation method makes it possible to increase by 15–20% the content of sulphides in the sulphuric acid concentrates[23].

Since aromatic hydrocarbons (benzene, naphthalene, and their homologues) do not enter into the ionic hydrogenation reaction even under severe conditions, the method can be used to hydrogenate the thiophens in aromatic sulphur compound concentrates, particularly since they can be obtained (see Section II) on treatment with any solvents which extract aromatic hydrocarbons selectively. Further separation of the aromatic and organosulphur compounds can be achieved by sulphuric acid extraction[16,18]. Two products of practical importance can be obtained by this procedure: sulphide concentrates and aromatic hydrocarbons.

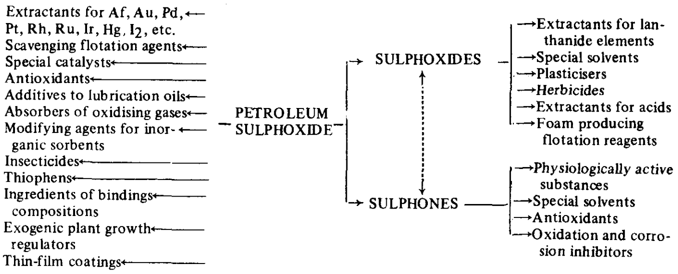


Figure 6. The applications of the sulphides in petroleum distillates; continuous arrows—tested on semi-industrial scale; dashed arrows—tested in the laboratory.

The ionic hydrogenation method is also promising for the conversion of thiophens directly in the distillates into the corresponding thiacycloalkanes, which are then extracted; this is particularly valuable in the study of the composition of the OSC in high-boiling petroleum distillates.

V. THE USE OF ORGANOSULPHUR COMPOUNDS OF PETROLEUM IN THE NATIONAL ECONOMY

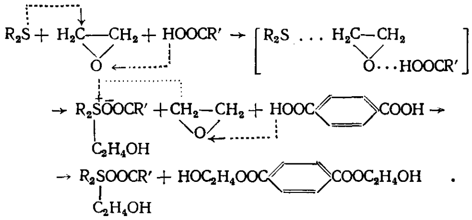
Studies of the compositions and properties of petroleum sulphides led to the discovery of their practical applications; in many instances large-scale industrial tests have been made (Fig.6). The oxidation of petroleum sulphides to sulphoxides and sulphones is of great practical importance; the preparation and properties of the latter have been examined in detail in a review[79]. It has been shown that sulphoxides can find extensive applications in hydrometallurgy and non-ferrous metallurgy as extractants and flotation agents. Studies in recent years have established that sulphoxides can be employed also in the chemical and petrochemical industry as effective solvents for phenols, resorcinol, catechol, hydroquinone[99], aromatic hydrocarbons[100], and acid oxides (SO_2, NO_2) contained in the waste gases released into the environment[101], and also as the starting materials for the synthesis of sulphones.

An extraction method has been developed for the elimination of monochloroacetic acid from sulphuric[102] and acetic[103] acids with the aid of sulphoxides. Sulphoxides have been tested successfully for the extraction of lower monocarboxylic acids from sewage[104] and of sulphur dioxide from industrial waste released into the atmosphere[105].

Some of the direct applications of petroleum sulphides are examined below.

1. Sulphides as Catalysts of the Oxidation of Terephthalic Acid

Individual OSC, for example thiacyclohexane[106], are known to be effective catalysts of the hydroxyethylation of terephthalic acid.



It has been shown[107] that petroleum OSC as well as thiacyclohexane are converted into a sulphonium salt by reaction with epoxyethane and terephthalic acid. The active complex obtained exhibits a high selectivity in the formation of bis-β-hydroxyethyl terephthalate.

OSC concentrates and purified sulphides isolated from petroleum distillates have been tested[23]. It has been found that an increase of the concentration of sulphide sulphur from 10.6 to 22.4% has a significant effect on the catalytic activity of sulphide concentrates, which is associated with the decrease of their content of thiophen derivatives. It has been noted that it is useful to obtain the sulphonium salts beforehand from OSC concentrates, epoxyethane, and terephthalic acid and then use them as catalysts.

A combined study has shown that the use of OSC concentrates (with $S_{\text{sulph}} \geqq 20\%$) in the stage involving the hydroxyethylation of terephthalic acid makes it possible to obtain poly(ethylene terephthalate) with satisfactory physicomechanical parameters.

2. Petroleum Sulphides as Highly Effective Extractants for Noble Metals

The complex formation reaction between the sulphides and various metal salts is of enormous practical importance for the concentration and separation of silver[108,109] and platinum-group metals[29]. The results of studies on the extraction of silver by petroleum sulphides of different structure have been published[108] and a virtually quantitative isolation of silver of high purity has been achieved.

The extraction of platinum metals by petroleum sulphides in the presence of cumenyl and pentyl hydroperoxide has been investigated and it has been shown that all platinum metals are extracted from hydrochloric acid solutions (0.5 to 5.0 M) with a high partition coefficient[29]. The dependence of the rate of extraction of platinum metals on the nature of the diluent has been established. The possibility of the selective separation of a mixture of noble metals in the regeneration stage has been demonstrated[29].

3. Petroleum Sulphides as Effective Flotation Agents

The possibility of using petroleum sulphides as scavenging reagents and foaming agents in the flotation of copper-nickel and copper-molybdenum sulphide ores has been studied[110-112]. The scavenging and foam-forming properties of sulphides have been compared with those of reagents widely used in flotation such as potassium butylxanthate and the T-66 foaming agent. It has been shown that the scavenging capacity of the sulphides approaches that of the xanthate and their foam-forming capacity is greater than that of the T-66 foaming agent. The boiling points of the sulphide fractions, i.e. their molecular weights, have little influence on the results of flotation. A decrease of the foam-forming capacity of sulphides with increasing boiling point has been observed. It has been shown that the use of petroleum sulphides for the enrichment of polymetallic sulphide ores increases the degree of extraction of non-ferrous and noble metals and greatly reduces the cost of flotation agents.

4. Petroleum Sulphides as Exogenic Regulators of the Growth of Gramineous Plants

Studies have shown a high effectiveness of sulphides as a non-root feed for rye and wheat[113]. It follows from the experimental data that sulphides have a positive influence on the assimilation of nitrogen by plants and also promote a more intense formation of proteins. Spraying of spring wheat and winter rye with a solution of sulphides increases the crop and the quality of the grain as well as the yield of protein per hectare. Supplementary feeding with petroleum sulphides increases the crop of certain varieties of wheat by 13.5%.

5. OSC Concentrates as Binding Additives to Soils

Organosulphur compounds exhibit an effective adhesion and it is therefore of interest to test them as additives to soils. Between 0.9 and 1.1% of the OSC concentrate was added to a composition of binding substances consisting of crude petroleum and cement. The results of tests showed that, when the amount of binding material containing added OSC is 9.1–11.15% of the mass of dry soil, the stability of the latter increases by 30–50% and the water-stability coefficient increases by 11–15% compared with soils stabilised with petroleum containing added cement[114]. Thus dusty sands stabilised by the binding material have effective physicomechanical properties.

---o0o---

In conclusion it must be emphasised that the study of the structural-group composition of the OSC of petroleum distillates is laborious and complicated. However, these investigations not only expand our ideas about the principal components of petroleums but, in combination with the development of industrial methods for their isolation, make it possible to create a scientific basis for the rational utilisation of the very rich store of organosulphur compounds which are of practical interest and are difficult to synthesise; they also permit the development, on the basis of studies of the chemical reactions of OSC, of methods of preparation of a wide variety of bifunctional and polyfunctional compounds of practical importance.

REFERENCES

1. G.D.Gal'pern, Uspekhi Khim., 1976, 45, 1395 [Russ.J. Chem.Rev., 1976(8)].
2. E.N.Karaulova, "Khimiya Sul'fidov Nefti" (The Chemistry of Petroleum Sulphides), Izd.Nauka, Moscow, 1970, p.202.
3. Ya.B.Chertkov and V.G.Spirkin, "Sernistye i Kislorodnye Soedineniya Neftyanykh Distillyatov" (The Sulphur and Oxygen Compounds in Petroleum Distillates), Izd.Khimiya, Moscow, 1973, p.307.

4. J.J.McKetta, Jr.(Editor), "Advances in Petroleum Chemistry and Refining", Interscience Publ., New York–London, 1960, Vol.3, p.125.
5. R.D.Obolentsev, "Sulfo-Organic Compounds in Oils of USSR. Proc.VII, World Petroleum Congr.London, 1968", p.110.
6. C.J.Thompson, H.J.Coleman, R.L.Hopkins, and H.T.Rall, Anal.Chem., 1968, **40**, 1562.
7. R.L.Hopkins, H.J.Coleman, and H.T.Rall, Anal.Chem., 1969, **41**, 2041.
8. H.T.Rall, C.J.Thompson, H.J.Coleman, and R.L.Hopkins, "Sulfur Compounds in Crude Oil", Washington USA, Bureau of Mines, Bulletin 659, 1972, p.187; Chem.Abs., 1973, **80**, 60 377.
9. N.K.Lyapina, M.A.Parfenova, T.S.Nikitina, A.A.Vol't-sov, and V.S.Nikitina, Neftekhimiya, 1979, **19**, 921.
10. K.I.Zimina, A.A.Polyakova, L.G.Siryuk, E.S.Brodskii, and E.A.Kalamashvili, in "Sostav Romashkinskoi Nefti" (The Composition of Romashki Petroleum), Prague, 1977, p.183.
11. J.E.Dooley, D.J.Hirsch, H.J.Coleman, and C.J.Thompson, USA Bureau of Mines, Bartes Ville Report of Investigation No.7821, p.30; Chem.Abs., 1974, **81**, 122 976.
12. J.E.Dooley, C.J.Thompson, D.J.Hirsch, and C.C.Ward, Hydrocarbon Process, 1974, **53**, 93.
13. C.J.Thompson, J.E.Dooley, I.W.Vogh, and D.Hirsch, Hydrocarbon Process, 1974, **53**, 193.
14. D.J.Hirsch, J.E.Dooley, and H.J.Coleman, USA Bureau of Mines, RJ—1974, No.7875, p.77; Chem.Abs., 1974, **81**, 108 165.
15. J.E.Dooley, D.J.Hirsch, C.J.Thompson, and C.C.Ward, Hydrocarbon Process, 1974, **53**, 187.
16. Ya.B.Chertkov, V.G.Spirkin, and V.N.Demishev, Neftekhimiya, 1965, **5**, 741.
17. M.A.Pais, V.S.Bogdanov, M.F.Bondarenko, and T.V.Portnova, Neftekhimiya, 1980, **20**, 607.
18. Ya.B.Chertkov and V.G.Spirkin, Neftekhimiya, 1968, **8**, 453.
19. M.F.Bondarenko, N.K.Lyapina, and A.S.Pon'kina, "Doklady Neftekhimicheskoi Sektsii. Materialy k Nauchno-proizvodstvennoi Konferentsii po Ekstraktsii i Adsorbtsii. Ufa, 1972" (Reports of the Petrochemical Section. Proceedings of the Scientific and Industrial Conference on Extraction and Adsorption, Ufa, 1972), No.6, p.62.
20. V.S.Nikitina, N.K.Lyapina, and A.D.Ulendeeva, Neftekhimiya, 1970, **10**, 594.
21. A.N.Plyusnin, V.I.Nesterenko, and T.A.Sagachenko, Neftekhimiya, 1976, **16**, 144.
22. G.L.Ryzhova, V.P.Nekhoroshev, and Yu.G.Slizhov, Neftekhimiya, 1977, **17**, 910.
23. V.S.Nikitina, N.K.Lyapina, F.G.Sattarova, N.S.Lyubopytova, and M.A.Parfenova, Neftekhimiya, 1971, **11**, 264.
24. I.U.Numanov, A.I.Skobelina, and B.I.Gizatova, Symposium, "Khimiya v Tadzhikistane" (Chemistry in Tajikistan), Izd.Donish, Dushanbe, 1974, p.121.
25. E.S.Brodskii, Kh.Khaitbaev, and S.L.Gusinskaya, Dokl.Akad.Nauk Uzbek.SSR, 1974, No.12, 26.
26. D.I.Kondakov, N.K.Lyapina, V.S.Nikitina, A.A.Smarkalov, Yu.E.Nikitin, and M.A.Parfenova, Symposium, "Khimiya i Fizika Nefti i Neftekhimicheskii Sintez" (The Chemistry and Physics of Petroleum and Petrochemical Synthesis), Izd.Bashkir.Fil.Akad.Nauk SSSR, Ufa, 1976, p.224.
27. L.K.Ezova, N.M.Ivanova, V.G.Spirkin, G.Z.Idiatullin, N.M.Lotareva, V.M.Germash, V.F.Gresev, A.Sh.Bashirov, and F.I.Arkhipov, Neftepererabotka i Neftekhimiya, 1966, No.10, 3.
28. Yu.E.Nikitin, Yu.I.Murinov, N.L.Egutkin, A.M.Rozen, N.Z.Mineeva, Yu.G.Kuvatov, and A.G.Kartavtseva, Symposium, "Khimiya i Fizika Nefti i Neftekhimicheskii Sintez" (The Chemistry and Physics of Petroleum and Petrochemical Synthesis), Izd.Bashkir.Fil.Akad.Nauk SSSR, Ufa, 1976, p.37.
29. G.V.Kuzmichev, N.K.Lyapina, Yu.E.Nikitin, L.P.Bulganina, Yu.I.Murinov, V.S.Kolosnitsyn, T.S.Makarova, and E.G.Kuzmichev, Symposium, "Neftekhimicheskii Sintez i Tekhnicheskii Progress (Tezisy Dokladov)" [Petrochemical Synthesis and Technical Progress (Abstracts of Reports)], Ufa, 1976, p.104.
30. E.N.Karaulova and G.D.Gal'pern, Dokl.Akad.Nauk SSSR, 1959, **124**, 583.
31. A.A.Khitrik, T.P.Burmistrova, R.M.Latypov, and G.D.Gal'pern, Trudy Kazan Khim.-Tekhnol.Inst., Kazan, 1972, **50**, 95.
32. E.N.Karaulova, B.A.Smirnov, and G.D.Gal'pern, Neftekhimiya, 1961, **1**, 339.
33. G.D.Gal'pern, T.S.Bobruiskaya, E.S.Brodskii, T.A.Bardina, E.N.Karaulova, R.A.Khmel'nitskii, and A.A.Polyakova, Neftekhimiya, 1970, **10**, 741.
34. I.U.Naumov, E.S.Brodskii, A.I.Skobelina, and R.A.Khmel'nitskii, Neftekhimiya, 1969, **9**, 776.
35. N.N.Kucheryavaya, L.G.Zherdeva, A.G.Siryuk, and O.A.Sladkovskaya, Khim.i Tekhnol.Topliv i Masel, 1974, No.6, 51.
36. A.M.Mazgarov, A.G.Akhmadullina, G.V.Tukov, V.A.Fomin, T.M.Vayush, B.V.Kizhaev, E.A.Veisman, and A.F.Fatkullina, Neftepererabotka i Neftekhimiya, 1975, No.5, 28.
37. R.L.Hopkins and H.M.Smith, Anal.Chem., 1954, **26**, 206.
38. R.D.Obolentsev, E.A.Makova, F.Sh.Ibragimova, and N.S.Lyubopytova, Neftekhimiya, 1970, **10**, 899.
39. V.D.Tyurin, S.P.Gubin, and N.S.Nametkin, IX World Petroleum Congr.Tokyo: Preprint, 1975, p.217.
40. M.A.Parfenova, E.S.Brodskii, K.I.Zimina, N.K.Lyapina, V.S.Nikitina, G.D.Kakabekov, A.A.Simeonov, and E.M.Kalamashvili, Neftekhimiya, 1975, **15**, 902.
41. L.A.Mel'nkova, N.K.Lyapina, and L.P.Karmanova, Neftekhimiya, 1980, **20**, 612.
42. L.A.Mel'nikova, L.P.Karmanova, N.K.Lyapina, A.A.Smarkalov, N.S.Lyubopytova, and T.S.Nikitina, Neftekhimiya, 1979, **19**, 273.
43. R.D.Obolentsev and A.Ya.Baikova, "Seraorganicheskie Soedineniya Neftei Uralo-Povolzh'ya i Sibiri" (The Organosulphur Compounds in the Petroleums of the Urals-Volga Region and Siberia), Izd.Nauka, Moscow, 1973, p.181.
44. M.A.Parfenova, N.K.Lyapina, E.S.Brodskii, and T.S.Nikitina, Neftekhimiya, 1977, **17**, 156.
45. M.A.Parfenova, N.K.Lyapina, T.S.Nikitina, and A.A.Smarkalov, Neftekhimiya, 1977, **17**, 315.
46. L.A.Mel'nikova, N.K.Lyapina, L.P.Karmanova, A.A.Smarkalov, and M.A.Parfenova, Neftekhimiya, 1978, **18**, 291.
47. S.S.Krivolapov, Abstract of Candidate's Thesis in Chemical Sciences, Bashkir State University, Ufa, 1968.
48. T.I.Allilueva, Abstract of Candidate's Thesis in Chemical Sciences, Bashkir State Univestity, Ufa, 1969.

49. V.Brown and S.Meyerson, Ind.Eng.Chem., 1952, **44**, 2620.
50. S.F.Birch and D.T.McAllan, J.Inst.Petrol., 1951, **37**, 443.
51. C.J.Thompson, H.J.Coleman, H.T.Rall, and H.M.Smith, Anal.Chem., 1955, **27**, 175.
52. S.F.Birch, T.V.Collum, R.A.Dean, and L.Denyer, Ind.Eng.Chem., 1955, **47**, 240.
53. W.S.Carruthers, Nature, 1955, **176**, 790, 4486.
54. F.P.Richter, K.L.Williams, and S.L.Meisel, J.Amer. Chem.Soc., 1956, **78**, 2166.
55. H.J.Coleman, C.J.Thompson, R.L.Hopkins, N.G.Foster, M.L.Whisman, and D.M.Richardson, J.Chem.Eng.Data, 1961, **6**, 464.
56. W.S.Carruthers and A.G.Douglas, J.Chem.Soc., 1964, **205**, 4077.
57. W.S.Carruthers and H.M.Stewart, J.Chem.Soc., 1967, **211**, 560.
58. M.A.Parfenova, N.K.Lyapina, E.S.Brodskii, V.S.Nikitina, and A.A.Smarkalov, Symposium, "Neftekhimicheskii Sintez i Tekhnicheskii Progress (Tezisy Dokladov)" [Petrochemical Synthesis and Technical Progress (Abstracts of Reports)], Ufa, 1976, p.51.
59. N.K.Lyapina, M.A.Parfenova, T.S.Nikitina, E.S.Brodskii, and A.D.Ulendeeva, Neftekhimiya, 1980, **20**, 619.
60. N.K.Lyapina, M.A.Parfenova, T.S.Nikitina, E.S.Brodskii, and A.D.Ulendeeva, Neftekhimiya, 1980, **20**, 747.
61. N.K.Lyapina, M.A.Parfenova, and A.D.Ulendeeva, Neftekhimiya, 1980, **20**, 908.
62. L.A.Mel'n7kova, Abstract of Candidate's Thesis in Chemical Sciences, Institute of Chemistry at the Bashkir Branch of the USSR Academy of Sciences, Ufa, 1980.
63. F.D.Rossini, B.J.Mair, and A.J.Streiff, "Hydrocarbons from Petroleum" (Translated into Russian), Gostoptekhizdat, Leningrad, 1957, p.365.
64. R.D.Obolentsev and A.V.Mashkina, "Gidrogenoliz Seraorganicheskikh Soedinenii Nefti" (Hydrogenolysis of the Organosulphur Compounds in Petroleum), Gostoptekhizdat, Leningrad, 1961, p.131.
65. R.D.Obolentsev, S.S.Krivolapov, T.I.Allilueva, G.V.Galeeva, V.S.Nikitina, R.L.Kaneva, and N.N.Lyushina, Symposium, "Khimiya Seraorganicheskikh Soedinenii, Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (The Chemistry of the Organosulphur Compounds in Petroleums and Petroleum Products), Izd.Vysshaya Shkola, Moscow, 1968, Vol.8, p.341.
66. A.I.Vorob'eva, S.Kh.Kiseleva, V.M.Gorina, M.A.Gurevich, and R.D.Obolentsev, Khim.i Tekhnol. Topliv i Masel, 1971, No.9, 12.
67. A.A.Anisonyan, N.M.Saltykova, and A.A.Zharova, Gaz.Prom., 1971, **11**, 40.
68. N.S.Nametkin, V.D.Tyurin, and M.A.Kukina, Neftekhimiya, 1978, **18**, 807.
69. A.S.Prochukhan, Abstract of Candidate's Thesis in Chemical Sciences, Bashkir State University, Ufa, 1968.
70. G.M.Prokhorov, R.V.Zainullina, A.S.Lukmanova, E.E.Zaev, N.S.Lyubopytova, V.I.Khvostenko, I.Kh.Aminev, and E.G.Galkin, Neftekhimiya, 1976, **16**, 285.
71. E.N.Prilezhaeva, T.E.Pivovarova, V.I.Snegotskii, V.Kh.Syundyukova, V.Z.Sharf, P.V.Saburova, A.L.Petunova, and V.A.Lukin, Symposium, "Khimiya Seraorganicheskikh Soedinenii, Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (The Chemistry of the Organosulphur Compounds in Petroleum and Petroleum Products), Izd.Vysshaya Shkola, Moscow, 1972, Vol.9, p.198.
72. M.F.Shostakovskii, E.N.Prilezhaeva, N.I.Uvarova, and V.M.Karavaeva, Symposium, "Khimiya Seraorganicheskikh Soedinenii, Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (The Chemistry of the Organosulphur Compounds in Petroleums and Petroleum Products), Izd.Akad.Nauk SSSR, Moscow, 1959, Vol.2, p.337.
73. G.A.Tolstikov, U.M.Dzhemilev, R.V.Kunakova, F.V.Sharipova, F.Ya.Kanzafarov, R.D.Gaisin, and Yu.A.Sangalov, Symposium, "Kataliticheskii Sintez Organicheskikh Soedinenii Sery" (Catalytic Synthesis of Organosulphur Compounds), Izd.Sibir.Otd.Akad. Nauk SSSR, Novosibirsk, 1979, p.15.
74. N.K.Lyapina, L.A.Mel'nikova, M.A.Parfenova, and A.D.Ulendeeva, Symposium, "IX Mezhdunarodnyi Simpozium po Khimii Organicheskikh Soedinenii Sery" (The IXth International Symposium on Chemistry of Organosulphur Compounds), Izd.Zinatne, Riga, 1980, p.328.
75. F.V.Whitehead, R.A.Dean, and F.A.Fidler, J.Amer. Chem.Soc., 1951, **73**, 3632.
76. L.B.Avdeeva and A.V.Mashkina, Neftekhimiya, 1974, **14**, 461.
77. G.V.Varnakova, L.M.Zagryatskaya, Z.A.Suleimanova, R.M.Masagutov, A.Kh.Sharipov, V.N.Yakovleva, L.A.Vlasova, N.P.Kirik, and A.V.Mashkina, Symposium, "Kataliticheskii Sintez Organicheskikh Soedinenii Sery" (Catalytic Synthesis of Organosulphur Compounds), Izd.Sibir, Otd.Akad.Nauk SSSR, Novosibirsk, 1979, p.66.
78. G.A.Kashafutdinov, F.N.Mazitova, and N.A.Iglamova, "Tezisy Dokladov XIV Nauchno Sessii po Khimii i Tekhnologii Organicheskikh Soedinenii Sery i Sernistykh Neftei" (Abstracts of Reports at the XIVth Scientific Session on the Chemistry of Technology of Organosulphur Compounds and Sulphurous Petroleums), Izd.Zinatne, Riga, 1976, p.70.
79. Yu.E.Nikitin, Yu.I.Murinov, and A.M.Rozen, Uspekhi Khim., 1976, **45**, 2233 [Russ.Chem.Rev., 1976(12)].
80. V.I.Dronov and R.S.Enikeev, Symposium, "Khimiya Seraorganicheskikh Soedinenii, Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (The Chemistry of the Organosulphur Compounds in Petroleums and Petroleum Products), Izd.Khimiya, Moscow–Leningrad, 1964, Vol.7, p.415.
81. R.D.Obolentsev, N.K.Lyapina, V.S.Nikitina, and M.A.Parfenova, Neftekhimiya, 1971, **11**, 125.
82. M.A.Parfenova, Abstracts of Candidate's Thesis in Chemical Sciences, Institute of Chemistry of the Bashkir Branch of the USSR Academy of Sciences, Ufa, 1978.
83. A.P.Lien and D.A.McCauley, Ind.Eng.Chem., 1949, **41**, 2698.
84. N.K.Lyapina, T.S.Nikitina, M.A.Parfenova, and G.P.Naletova, "Tezisy Dokladov II Neftekhimicheskogo Simpoziuma Sotsialisticheskikh Stran, Leiptsig, 1980" (Abstracts of Reports at the IInd Petrochemical Symposium of Socialist Countries, Leipzig, 1980), p.70.
85. R.D.Obolentsev, V.G.Bukharov, and N.K.Faizullina, Symposium, "Khimiya Sera- i Azotorganicheskikh Soedinenii, Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (The Chemistry of the Organosulphur and Organonitrogen Compounds in Petroleums and Petroleum Products), Izd.Bashkir.Fil.Akad.Nauk SSSR, Ufa, 1960, Vol.3, p.51.
86. I.V.Goncharov, Yu.P.Turov, N.P.Eletskii, and A.N.Plyusnin, Neftekhimiya, 1976, **16**, 149.

87. G.L.Ryzhova, A.A.Polyakova, V.P.Nekhoroshev, L.O.Kogan, and Yu.T.Slizhov, Symposium, "Mineral'noe Syr'e i Neftekhimiya" (Minerals and Petrochemistry), Tomsk, 1977, p.136.
88. E.A.Viktorova, M.V.Vagabov, T.A.Danilova, and E.A.Karakhanov, Symposium, "Kataliticheskii Sintez Organicheskikh Soedinenii Sery" (Catalytic Synthesis of Organosulphur Compounds), Izd.Sibir.Otd.Akad. Nauk SSSR, Novosibirsk, 1979, p.115.
89. V.P.Gvozdetskaya, Zhur.Prikl.Khim., 1977, **50**(4), 900.
90. A.A.Rozhdestvenskaya, B.B.Krol', and N.P.Kucheryavaya, "Trudy VNIINP: Metody Issledovanii Neftei i Nefteproduktov" (Transactions of the All-Union Institute of Petroleum Products: Methods for the Investigation of Petroleums and Petroleum Products), Izd.Khimiya, Moscow, 1967, No.10, p.121.
91. R.A.Virobyants, V.K.Gonik, G.F.Tarasova, R.R.Shagidullin, and F.K.Sattarova, Symposium, "Khimiya Seraorganicheskikh Soedinenii, Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (The Chemistry of the Organosulphur Compounds in Petroleums and Petroleum Products), Izd.Khimiya, Moscow–Leningrad, 1964, Vol.6, p.35.
92. Ya.B.Chertkov, V.G.Spirkin, and V.N.Demishev, Neftakhimiya, 1966, **6**, 309.
93. R.J.Emmott, Inst.Petrol., 1953, **39**, 695.
94. R.L.Martin and J.A.Grant, Anal.Chem., 1965, **37**, 644.
95. R.N.McCoy and F.T.Weiss, Anal.Chem., 1954, **26**, 1928.
96. P.G.Klaas, Anal.Chem., 1961, **33**, 1851.
97. D.N.Kursanov and Z.N.Parnes, Uspekhi Khim., 1969, **38**, 1783 [Russ.Chem.Rev., 1969(10)].
98. N.K.Lyapina, Z.N.Parnes, G.A.Tolstikov, and M.A.Parfenova, "Tezisy Dokladov XV Nauchnoi Sessii po Khimii i Tekhnologii Organicheskikh Soedinenii Sery i Sernistykh Neftei. Ufa, 1979" (Abstracts of Reports at the XVth Scientific Session on the Chemistry and Technology of Organosulphur Compounds and Sulphurous Petroleums, Ufa, 1979), p.44.
99. Yu.E.Nikitin, N.L.Egutkin, and I.P.Malaya, "Tezisy Dokladov XV Nauchnoi Sessii po Khimii i Tekhnologii Organicheskikh Soedinenii Sery i Sernistykh Neftei. Ufa, 1979" (Abstracts of Reports at the XVth Scientific Session on the Chemistry and Technology of Organosulphur Compounds and Sulphurous Petroleums, Ufa, 1979), p.50.
100. O.A.Kolyadina, Yu.I.Murinov, and Yu.E.Nikitin, Symposium, "IX Mezhdunarodnyi Simpozium po Khimii Organicheskikh Soedinenii Sery" (The IXth International Symposium on Chemistry of Organosulphur Compounds), Izd.Zinatne, Riga, 1980, p.212.
101. G.G.Bikbaeva, Yu.E.Nikitin, and E.M.Baranovskaya, "Tezisy Dokladov XV Nauchnoi Sessii po Khimii i Tekhnologii Organicheskikh Soedinenii Sery i Sernistykh Neftei. Ufa, 1979" (Abstracts of Reports at the XVth Scientific Session on the Chemistry and Technology of Organosulphur Compounds and Sulphurous Petroleums, Ufa, 1979), p.30.
102. Yu.E.Nikitin, N.L.Egutkin, Yu.I.Murinov, and N.K.Lyapina, USSR P.466 182 (1973); Byul.Izobret., 1975, No.13, 46.
103. Yu.E.Nikitin and N.L.Egutkin, Zhur.Prikl.Khim., 1977, **50**, 2118.
104. Yu.E.Nikitin and N.L.Egutkin, Neftekhimiya, 1974, **14**, 780.
105. Yu.I.Murinov, O.A.Kolyadina, and Yu.E.Nikitin, USSR P.606 606 (1976); Byul.Izobret., 1978, No.18, 13.
106. S.A.Babets, S.Khushvakhtova, V.A.Malykh, A.S.Chegolya, and E.A.Viktorova, Zhur.Prikl.Khim., 1976, **49**, 402.
107. S.A.Babets, S.Khushvakhtova, V.A.Malykh, A.S.Chegolya, V.A.Viktorova, and N.K.Lyapina, Zhur.Prikl.Khim., 1976, **49**, 209.
108. A.V.Nikolaev, V.G.Torgov, V.A.Mikhailov, V.N.Andrievskii, K.A.Bakovets, M.F.Bondarenko, E.N.Gil'bert, I.L.Kotlyarovskii, G.A.Mardezhova, and S.S.Shatskaya, Izv.Sibir.Otd.Akad.Nauk SSSR, Ser.Khim.Nauk, 1970, **4**(9), 54.
109. A.M.Rozen, V.S.Nikitina, and N.K.Lyapina, Radiokhimiya, 1972, **14**, 582.
110. A.V.Bocharov, N.V.Filimonov, Yu.E.Nikitin, and V.S.Nikitina, Tsvetnye Metally, 1970, No.11, 36.
111. G.V.Kuzmichev, Yu.E.Nikitin, N.K.Lyapina, and A.V.Smyshlyaeva, Symposium, "Neftekhimicheskii Sintez i Tekhnicheskii Progress (Tezisy Dokladov)" [Petrochemical Synthesis and Technical Progress (Abstracts of Reports)], Ufa, 1976, p.103.
112. I.U.Numanov, G.D.Gal'pern, E.N.Karaulova, and L.I.Skobelina, Symposium, "Khimiya Seraorganicheskikh Soedinenii, Soderzhashchikhsya v Neftyakh i Nefteproduktakh" (The Chemistry of the Organosulphur Compounds in Petroleums and Petroleum Products), Izd.Vysshaya Shkola, Moscow, 1968, p.397.
113. G.E.Radtseva, N.K.Lyapina, N.N.Ryakhovskaya, and K.B.Sakaeva, USSR P.629 211 (1977); Byul. Izobret., 1978, No.39, 88.
114. Yu.N.Bogomolov, Abstract of Candidate's Thesis in Technical Sciences, Leningrad Institute of Civil Engineering, Leningrad, 1980.

Institute of Chemistry of the
Bashkir Branch of the USSR
Academy of Sciences