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DEMERCAPTANIZATION OF FUELS AND LIQUEFIED GASES IN THE PRESENCE OF COBALT POLYPHTHALOCYANINE

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Because of the increasing volumes of crudes and gas condensates with high mercaptan sulfur contents that are now being produced, it has become necessary to adopt new, highly effective methods for treating fuels to remove mercaptan compounds. The mercaptan content is a major factor in determining the reliability of operation of engine fuel systems. High contents of mercaptans have adverse effects on the thermal stability and corrosivity of the fuel; other adverse effects are the bad odor and the greater amounts of deposits formed on the surface of parts in the engine system. Therefore, the content of mercaptan sulfur in TS-1 and RT jet fuels (GOST 10227-86) is restricted to 0.005% and 0.001%, respectively, and the content in diesel fuel (GOST 305-82) to 0.01% [1].

The volatile mercaptans that are present in LPG have an unpleasant odor. For example, ethyl mercaptan in air can be detected by its odor at a concentration of only $2 \cdot 10^{-6}$ mg/liter. Such gases should be stored in vapor-type tanks under pressure. The lower aliphatic mercaptans cause severe metal corrosion. According to [2], even octyl mercaptan (0.1% by weight), in the presence of moisture at 70°C for 4 h, causes corrosion of a steel strip amounting to 11.4 g/m^2. In this connection, cross-country pipelines carrying gas condensate that contains mercaptans, and also equipment used in processing such condensate, must be fabricated from expensive high-alloy steel. In order to avoid corrosion of equipment and pipelines, the content of mercaptan sulfur in commercial gasoline should be limited to 0.01% by weight [3].

In the petroleum refining industry, hydrotreating is widely used to remove mercaptans from distillates (this is the basic method for producing high-quality fuels from medium-sulfur crudes); selective demercaptanization processes are also used. Catalytic hydrotreating is the most effective method. However, the available hydrotreating capacity is insufficient to treat all of the fuels produced in refineries. Further, the influence of the degree of hydrotreating on the service properties of fuels, particularly jet fuels, has not been investigated adequately. Therefore, the advantage sometimes lies on the side of selective demercaptanization, which is simple in terms of the process flow plan and quite inexpensive.

From experience accumulated in lube oil production, it is known that removal of natural antioxidants along with the harmful components will have an adverse effect on the stability of the oil. Analogous results may be obtained when treating fuels, since consumers tend to demand the greatest possible degree of removal of sulfur compounds. In comparison with our standards, foreign standards allow a higher content of total sulfur in jet fuels (up to 0.4%, in comparison with 0.25% in our standards), and also allow for the introduction of antioxidants and metal deactivators [4]. It has also been established that diesel fuels with total sulfur contents of 0.2-0.3% — if mercaptans, hydrogen sulfide, and free sulfur are absent — are 10 times more stable than completely desulfurized fuels [5, 6].

Absorption in aqueous solutions is one of the effective methods for treating liquid and gaseous hydrocarbons to remove low-boiling mercaptans [7]. The effectiveness of this method is determined by the acidic properties of the mercaptans. The acidity decreases with increasing molecular weight of the mercaptan, and also decreases in the series from primary to secondary and tertiary mercaptans. One of the disadvantages of caustic extraction is the reversibility of the reactions between the mercaptans and the caustic: As mercaptans continue to accumulate in the caustic solution, an equilibrium is established, preventing any further extraction of mercaptans. Other disadvantages are the large consumption of soda materials (which are in short supply) and the formation of large amounts of sour caustic waste, the collection and treatment of which add considerably to the processing cost.

The technoeconomic indexes of the caustic treating process are improved by regenerating the spent caustic for reuse in a closed cycle. Various methods of regeneration have been proposed; of the greatest interest from the practical point of view

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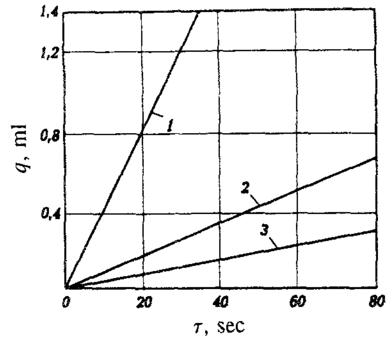

Fig. 1. Quantity of oxygen absorbed q as a function of oxidation time τ: 1) *n*-amyl mercaptan; 2) thiophenol; 3) *tert*-amyl mercaptan.

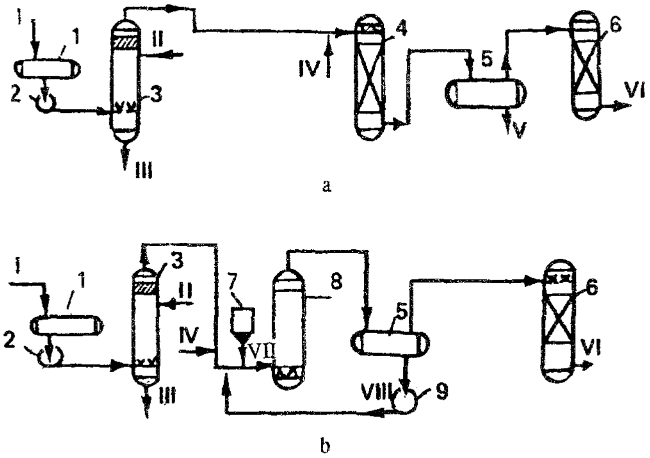

Fig. 2. Flow plan of unit for demercaptanization of thermal naphthas (*a*) and catalytic naphthas (*b*): *1)* receiving tank; *2,9)* pumps; *3)* column for preliminary caustic washing; *4)* reactor with solid catalyst; *5)* caustic settler; *6)* sand filter; *7)* tank with catalyst; *8)* mixer; *I)* naphtha; *II,III,VIII)* fresh, spent, and circulating caustic, respectively; *IV)* air for oxidation; *V)* caustic entrained with catalyst; *VI)* treated naphtha; *VII)* addition of catalyst.

is the oxidation of mercaptans to disulfides by atmospheric oxygen in the presence of certain catalysts that act as oxygen carriers [8, 9].

Mercaptans that are only slightly soluble in caustic can be eliminated by direct oxidation in the fraction being treated. It is impossible to remove any significant amounts of these mercaptans from gasoline or kerosine by caustic extraction when the distribution between the caustic and the hydrocarbons reaches equilibrium. However, these mercaptans are sufficiently soluble that they will enter into the caustic phase to a limited degree. It may be that only the SH group enters into the caustic phase. In this case, in the presence of a special catalyst and air, the mercaptan molecule is instantly oxidized to a disulfide. This description of the oxidation mechanism is highly simplified, but it provides a graphic illustration of the possibility, under certain conditions, of transforming unextractable mercaptans into less active compounds - disulfides. The oxidation is performed in an alkaline medium. The oxidation catalyst may be deposited on a stationary solid support, or it may be suspended in the caustic solution.

The usual catalysts for such processes are caustic solutions of phthalocyanine complexes, primarily cobalt and iron complexes [10, 11]. With these catalysts, demercaptanization is carried out at 40-80°C under atmospheric pressure. The process pressure is ordinarily determined by the vapor pressure of the product being treated and by the hydraulic resistance of the system.

TABLE 1

Catalyst	Quantity of catalyst, wt. %	Time required for oxidation of 90% of the *n*-butyl mercaptan, min
Phthalocyanine		
cobalt	0,2	20
copper	0,2	19
iron	0,2	49
Polyphthalocyanine		
cobalt	0,2	2
	0,1	4
copper	0,1	4

TABLE 2

Catalyst	pH of solution	Specific activity of catalyst ($\times 10^{-5}$, ml O_2/(g·min	Rate of oxygen absorption, ml/min	Hydrogen sulfide conversion, %
Phosphomolybdic/vanadic acid	1,1	15	0,15	90
Copper chloride	9,5	21	0,18	92
Cobalt sulfophthalocyanine	9,5	50	0,5	100
Cobalt polyphthalocyanine	9,5	116	1,2	100

A search is being made for new, more effective catalysts. Bifunctional catalysts have been developed, with which it is possible to eliminate or minimize the use of the caustic agent. Polymeric forms of the cobalt and iron compounds are of great interest, as they are an order of magnitude more active than the monomeric forms [12, 13]. In the pilot plant of NIIneftekhim [Scientific-Research Institute of Petroleum Chemistry], a process for the manufacture of cobalt polyphthalocyanine has been developed and put into operation [14]. This material is produced under the trade name Okmer, for the demercaptanization of naphthas and kerosines [15] and LPG [16].

In this article we have systematized and correlated results from research studies and commercial experience in the manufacture and use of cobalt polyphthalocyanine in treating fuels and gases to remove mercaptan compounds.

Catalytic Properties of Metal Polyphthalocyanines in Mercaptan Oxidation Reactions

It was shown in [12] that cobalt, copper, and iron polyphthalocyanines with a degree of polymerization 6-7 exhibit high catalytic activities in the oxidation of mercaptan compounds. They are used in caustic solutions in amounts of 0.001% to 0.2% by weight. In Table 1 we present results obtained with polyphthalocyanine catalysts in comparison with phthalocyanine catalysts, in the oxidation of *n*-butyl mercaptan.

A study has been made to determine how the polymeric state of the ligand influences the catalytic activity of phthalocyanines of various metals in the oxidation of cysteine and *n*-, *iso*-, and *sec*-butyl mercaptans [13]. The polyphthalocyanines of nontransition metals do not catalyze these reactions. The most active catalysts are the polymeric complexes of cobalt and iron. The reaction rate is highly dependent on the length and degree of branching of the hydrocarbon radical in the mercaptan molecule [17]. As can be seen from Fig. 1, when using the cobalt polyphthalocyanine, the highest rate of oxidation is observed for the *n*-amyl mercaptan. Branching of the hydrocarbon chain results in a much slower reaction: The initial rate of oxidation of *tert*-amyl mercaptan is several times lower. An aromatic mercaptan, thiophenol, is intermediate between the *n*- and *tert*-amyl mercaptans in oxidation rate. Polymeric catalysts on a support are more active than unsupported catalysts, if the activity is calculated per unit of active phase.

Activities have been compared for cobalt polyphthalocyanine and cobalt sulfophthalocyanine in the oxidation of mercaptans to disulfides and the oxidation of hydrogen sulfide to sulfur [18]. The oxidation rates for the mercaptans and also

TABLE 3

Mercaptan compound	Oxidation time, min	Conversion to disulfide, %
n-Butyl mercaptan	7/3	99,1/100
n-Dodecyl mercaptan	11/4	98,7/100
tert-Amyl mercaptan	41/24	97,6/99,9
Thiophenol	33/18	98,5/99,6

Notes: 1) Content of mercaptan sulfur in feed 2588 ppm. 2) First value is with cobalt polyphthalocyanine, second value with a 1/1 mixture with cobalt poly(butyl mercaptide).

for hydrogen sulfide are 2-2.5 times higher when using the cobalt polyphthalocyanine. On the basis of these data, a process has been developed [19, 20] for treating gases to remove mercaptans and hydrogen sulfide, using as the absorption agent aqueous caustic solutions that are subsequently regenerated by atmospheric oxygen in the presence of cobalt polyphthalocyanine. The process provides thorough extraction (more than 99%) of the mercaptans and hydrogen sulfide from natural gas, followed by catalytic conversion of these compounds to disulfides and sulfur. In subsequent work, the process for elimination of hydrogen sulfide from gas was improved [21]. The recommended absorption agent in the improved process is an aqueous solution of a nitrogen-containing compound with both amine and amide groups in the molecule (or with these groups and others). The absorbent is regenerated by blowing with air, using cobalt polyphthalocyanine supported on activated carbon. The degree of regeneration of the absorption agent is as high as 99.9%, with no loss of catalyst.

In Table 2 we illustrate the performance of different types of catalyst as measured by the rate of oxygen absorption, the specific activity of the catalyst, and the degree of hydrogen sulfide conversion. It will be seen that in this case also, the cobalt polyphthalocyanine is distinguished by high activity.

A study has been made of the influence of catalyst concentration on the degree of hydrogen sulfide conversion at 25°C in aqueous solutions of diethanolamine and dimethylformamide at pH 9.5. With a cobalt polyphthalocyanine concentration of 80 mg/liter, the absorbed hydrogen sulfide is almost completely converted. When cobalt sulfophthalocyanine is used, total conversion of hydrogen sulfide is achieved only with a catalyst concentration of 200 mg/liter. These results have been confirmed in the operation of experimental-commercial units. The process is highly efficient, reliable, and flexible in operation [22, 23].

Good results have been obtained in treating a butane-butene fraction to eliminate mercaptans, using cobalt polyphthalocyanine catalyst [16]: The content of mercaptan sulfur in the treated fraction was found to be below 0.0003% by weight.

Another major advantage of this catalyst is the possibility of treating feedstocks with high contents of mercaptan sulfur. For the demercaptanization of kerosine, the cobalt polyphthalocyanine is used in a fixed bed [15]. The support is an activated carbon, Grade AG-3 or SKT. Straight-run aviation kerosine treated by this method gives a negative doctor test, and there is no adverse effect on the color.

Cobalt phthalocyanine readily forms monoadducts and bisadducts; the ligand that is coordinated in the axial position has a significant effect on the catalytic properties of the material [24]. When certain compounds of nitrogen and oxygen are added to a system containing an aqueous caustic solution of cysteine and cobalt phthalocyanine, the reaction rate is greatly changed [25]. This effect is explained by the formation of adducts by interaction of the cobalt phthalocyanine and the added compounds, these adducts differing substantially from the original cobalt phthalocyanine in their catalytic activity. Cobalt polyphthalocyanine behaves similarly.

In [17], it was shown that the rate of mercaptan oxidation was increased by the combined use of cobalt polyphthalocyanine and poly(butyl mercaptide) (Table 3). Complete (100%) elimination of mercaptans was achieved for not only the low-boiling mercaptans, but also the difficultly oxidized high-boiling, tertiary aliphatic, and aromatic mercaptans. The oxidation rates in the presence of the cobalt polyphthalocyanine and the cobalt poly(butyl mercaptide) were 2.0-2.5 times those when only the cobalt polyphthalocyanine was present.

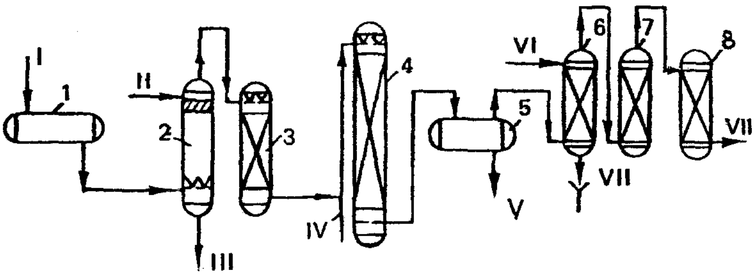

Fig. 3. Flow plan of unit for demercaptanization of kerosine: *1*) receiving tank; *2*) caustic wash column; *3*) sand filter; *4*) reactor with solid catalyst; *5*) caustic settler; *6*) water wash column; *7*) salt filter; *8*) clay filter; *I*) kerosine; *II,III*) fresh and spent caustic, respectively; *IV*) air; *V*) caustic entrained with catalyst; *VI,VII*) fresh and contaminated water, respectively; *VIII*) treated kerosine.

In certain kerosine fractions from crude oils and gas condensates, the mercaptan compounds are represented by difficultly oxidized tertiary aliphatic and aromatic mercaptans. For such products, therefore, the use of the treating method described above is fully justified. Oxidation of the feed by atmospheric oxygen is performed in an aqueous caustic solution in the presence of cobalt polyphthalocyanine and poly(butyl mercaptide) in a weight ratio of 1.0/0.8 to 1.0/2.5. The two catalysts may be introduced into the system directly, or they may be first deposited together on an activated carbon support. With these catalysts, the feedstock is almost completely freed of not only low-boiling mercaptans, but also high-boiling, tertiary aliphatic, and aromatic mercaptans that are difficult to remove.

From the data we have presented, it can be seen that cobalt polyphthalocyanine is a highly effective catalyst for the demercaptanization of petroleum distillates and gases. When this catalyst is used, there are broad possibilities for controlling the rate and selectivity of mercaptan oxidation by the introduction of additives.

Commercial Experience in the Use of Cobalt Polyphthalocyanine

This catalyst is used for the treatment of thermal naphthas and kerosines [15], butane-butene fractions [16], and pentanes [26]. In the following material we will examine demercaptanization processes as applied to various petroleum products, and also the prospects for expanded application of these processes.

Demercaptanization of Naphthas

The use of this process is advisable in treating naphthas containing no more than 0.2% total sulfur, in refineries processing medium-or low-sulfur crudes, without any facilities for hydrotreating secondary naphthas. It is also possible to treat naphthas with higher contents of total sulfur if the final commercial gasoline blend does not contain too great a percentage of this naphtha. The reason for these restrictions is that the total sulfur content is not reduced by the demercaptanization process.

In worldwide practice, hydrotreated cracked naphthas are not subjected to demercaptanization; but cracked naphthas obtained from hydrotreated feedstocks are demercaptanized in order to improve their commercial properties (odor) [27]. In a number of cases, when processing crudes with a low content of total sulfur, instead of preliminary hydrotreating of the cat cracker feed, it may be better to demercaptanize the catalytic naphthas if their total sulfur content is no greater than 0.15-0.25%. By these means, the costly process of vacuum distillate hydrotreating can be eliminated, and naphthas with higher chemical stability can be obtained, without any unpleasant odor.

In straight-run naphthas with comparatively low contents of total sulfur, the mercaptan sulfur content may be as great as 0.03%, sometimes even 0.06%. In the new standard being developed for naphthas, a new index will be included: mercaptan sulfur content no greater than 0.01%. Consequently, such naphthas, particularly those for export, must be demercaptanized.

In naphthas after demercaptanization, without any removal of phenols, the content of mercaptan sulfur must not be greater than 0.0005% by weight, gum content 5 mg/liter. It should be noted that selective demercaptanization produces hardly any changes in the fuel property indexes other than the mercaptan sulfur content. In terms of technoeconomic indexes, this process has no equal. The naphtha treating cost and the capital costs per tonne of feedstock are lower than in hydrotreating in an L-24-14B unit, by 96% and 94%, respectively [28].

Flow plans for the demercaptanization of thermal and catalytic naphthas are shown in Figs. *2a* and *2b*, respectively. In treating the thermal naphtha, which has a higher mercaptan content, a more active fixed bed of the catalyst is used - cobalt polyphthalocyanine, deposited by a special method on activated charcoal that has already been charged to the reactor. After completing the impregnation of the charcoal with the cobalt polyphthalocyanine, the reactor is filled with a sodium hydroxide solution for a certain time in order to saturate the catalyst with caustic. The excess caustic solution is drained into the settler. When the draining has been completed and the preliminary caustic wash column has been charged with a 6-8% caustic solution, the unit is ready for operation.

Naphtha from the thermal cracking unit passes directly into the receiving tank of the demercaptanization unit (Fig. *2a*). If the demercaptanization unit is shut down for maintenance, incoming naphtha is directed to an auxiliary tank after washing and inhibiting. The inhibitor - Ionol or phenylenediamine - is introduced in order to prevent oxidation and the formation of peroxide compounds. The caustic wash removes hydrogen sulfide and thiophenol, which are activators of peroxide formation — the first stage in gum formation.

If the oxidation process with the formation of peroxide compounds has already begun, inhibitors cannot prevent the further development of the process. In this case, the naphtha from the receiving tank is pumped to the pretreating column, where it is contacted with a sodium hydroxide solution to remove hydrogen sulfide and aliphatic acids. If the naphtha does not contain any hydrogen sulfide and only small amounts of aliphatic acids, the preliminary wash operation is not necessary. After the preliminary washing, the naphtha is doped with 0.03-0.20 kg/tonne of a caustic-insoluble inhibitor - Ionol.

The prewashed and inhibited naphtha is mixed with air and then passes downward through the reactor, contacting the cobalt polyphthalocyanine on a support saturated with caustic soda. During the course of the reaction, an excess pressure of 1.8-2.0 MPa is established in order to hold the air in the naphtha in the dissolved state. If a separate air phase is present in the reactor, channeling takes place: The air proceeds through one channel, the naphtha through another.

Demercaptanization is accomplished in the reactor. The treated naphtha, together with a certain quantity of sodium hydroxide solution, is drained from the catalyst bed, passes into a side collector located below the reactor, and then passes into the caustic settler. After the settler, the naphtha may still contain a small amount of a stable "mist" of caustic solution. In the sand filter, the mist is collected in the form of large drops and then separated. From time to time, the catalyst bed must be resaturated with caustic. To do this, the caustic is pumped from the settler to the top of the reactor without interrupting the naphtha flow. From the sand filter, the bright, demercaptanized naphtha passes to commercial product tanks.

Catalytic naphtha is treated by liquid-phase extraction in the presence of cobalt polyphthalocyanine (see Fig. *2b*). From the receiving tank, the naphtha is pumped to the prewash column, where traces of hydrogen sulfide are removed by treatment with a 4-6% caustic solution. Before the prewashing, 0.01-0.06 kg/tonne of a caustic-insoluble antioxidant (Ionol) is added to the naphtha. After washing, the naphtha is mixed with air in a twice-stoichiometric quantity and with a 6-10% caustic solution (solution volume 12-15% of naphtha volume), after which the stream passes into a mixer containing a sequence of nine metering orifices, positioned in a vertical line.

The naphtha, caustic, and air are brought into good contact by the turbulence created as they flow through the orifices. The mercaptan passes into the caustic phase and is oxidized to disulfide. The disulfide is transferred to the naphtha phase, since it is insoluble in the caustic solution. The products remain in the mixer for a time sufficient to complete the reaction. From the mixer, the components pass to the settler for separation of the caustic solution, which is then pumped back to the mixer. The caustic solution circulating through the mixer contains 0.003-0.006% cobalt polyphthalocyanine catalyst. Makeup catalyst is added to the system periodically through a specially designed tank *7*. A gauge pressure of 0.8-1.0 MPa is maintained in the system.

The naphtha leaving the settler may contain extremely fine particles of caustic solution in the form of a mist. Therefore, it is directed to a sand filter, in which the entrained particles are coalesced, forming large drops that can be readily separated. After the filter, the treated naphtha passes to a commercial product tank.

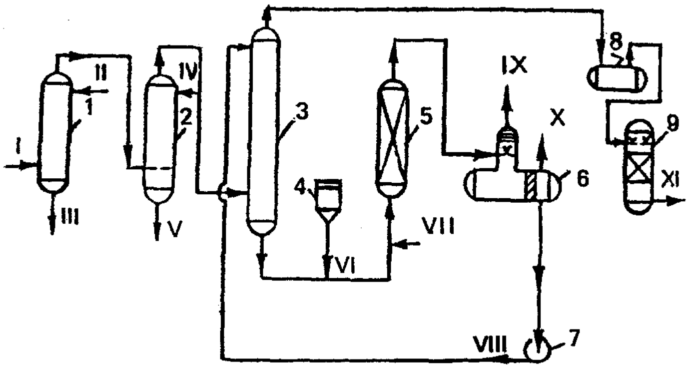

Fig. 4. Flow plan of unit for demercaptanization of butane–butene fraction: *1,2*) columns for treatment to remove hydrogen sulfide and for caustic wash, respectively; *3*) mercaptan extractor; *4*) tank with catalyst; *5*) oxidizer column; *6*) disulfide settler; *7*) pump; *8*) caustic settler; *9*) sand filter; *I*) butane–butene fraction; *II*) amine; *III*) amine to regeneration; *IV, V, VIII*) fresh, spent, and circulating caustic, respectively; *VI*) addition of catalyst; *VII*) air for oxidation; *IX*) blowoff of gas to flare; *X*) disulfides; *XI*) treated butane–butene fraction.

Demercaptanization of Kerosine

In other countries, the Merox process is used extensively in treating straight-run aviation kerosines. This process is the most economical means of treating kerosines that meet all requirements of the standards with the exception of the mercaptan content [29].

Demercaptanized straight-run kerosine from medium-sulfur Russian crudes is characterized by a low content of mercaptan sulfur, no acidity, low corrosivity, and high thermal stability under dynamic conditions. According to data obtained by VNII NP [All-Russian Scientific-Research Institute for Petroleum Processing], these materials meet the GOST standard requirements for TS-1 fuel, and also meet all requirements for RT fuel except the thermal stability under static conditions. The production of RT fuel requires the use of an additive to improve the thermal stability under static conditions. As the base fuel it would be possible to use a mixture of hydrotreated and demercaptanized components with an additive to improve the thermal stability. Unfortunately, no such additive has yet been developed; therefore, the kerosine demercaptanization process can be used only for the production of TS-1 from medium-sulfur crudes by blending straight-run [hydrotreated] and demercaptanized components.

In refineries processing crudes with a low content of total sulfur, the use of demercaptanization will make it possible to reduce the hydrotreating capacity needed to obtain blended TS-1 fuel. The same as for naphthas, the costs for demercaptanization of kerosine are much lower than for hydrotreating [15]. The demercaptanization process is distinguished by simple mechanical design; as a consequence, the capital investment in constructing the unit is only one-twelfth that for constructing a hydrotreating unit, and the cost for demercaptanizing kerosine is 7% lower than for hydrotreating.

Demercaptanization is performed at comparatively low temperatures. Therefore, there is virtually no breakdown of the fuel, and very little loss. For example, in a demercaptanization unit with a capacity of 500 thousand tonnes/yr, the loss of kerosine is 2.5 thousand tonnes/yr, in comparison with 13.5 thousand tonnes/yr in a hydrotreating unit. In view of the shortage of jet fuels, an increase of their potential resources by 11 thousand tonnes/yr by the elimination of hydrotreating is a very significant factor. Kerosine obtained by the use of polyphthalocyanine catalyst meets all requirements in the official tests included in the set of methods for qualifaction evaluation of service properties, as performed at VNII NP.

It should be noted that the kerosine demercaptanization process with cobalt polyphthalocyanine is comparable in technical level to foreign processes using cobalt and vanadium phthalocyanine catalysts [31].

In Fig. 3 we show a flow plan of a unit for kerosine treating. Kerosine from an atmospheric distillation tower passes into the receiving tank of the demercaptanization unit, from which it is pumped to the caustic prewash column, where it is treated with a 1.1% caustic soda solution. Here the hydrogen sulfide and naphthenic acids react with the caustic and are removed from the kerosine. The washed kerosine passes through a sand filter to remove the sodium naphthenate particles left in the fuel. After the filter, air is injected into the kerosine by means of a specially designed device. The system pressure is held at a level high enough to dissolve air in the kerosine, in order to avoid two-phase flow in the reactor and the formation of local flow breakthrough.

The solution of air in kerosine in the reactor moves from top to bottom through a fixed bed of catalyst impregnated with a 12% caustic soda solution. Mercaptan compounds are eliminated from the kerosine upon contact with the fixed bed of catalyst in the presence of atmospheric oxygen and caustic. Here the air is used only in an amount sufficient to oxidize the mercaptans. Any excess air would be consumed in oxidizing phenolic and nitrogen-containing compounds, resulting in the formation of colored components.

Caustic is gradually entrained from the fixed bed of catalyst with the kerosine and carried over to the settler, where it is retained. A certain quantity of caustic remains in the kerosine leaving the settler, in the form of fine particles. This caustic is removed in a water wash column. The washing also removes water-soluble surfactants. After the water wash, the kerosine passes through a salt filter to remove water. The dehydrated kerosine then passes into two parallel clay filters to remove copper and the surfactants that are insoluble in water, as well as those that are soluble but were not removed by the water wash.

Demercaptanization of Liquefied Gases

The place of this stage in the flow plan depends on the content and nature of the mercaptan compounds and also on the end-use of the liquefied gas [31]. It is sometimes advisable to demercaptanize the entire gas mixture before it enters the gas fractionation unit. After monoethanolamine treatment and before the demercaptanization section, the LPG stream must be post-treated with caustic soda solution to remove residues of hydrogen sulfide.

It is known that the greatest quantity of caustic soda is consumed in removing mercaptan compounds from feedstocks for alkylation, i.e., butane–butene and propane–propene fractions. On the average, the treatment of 1 tonne of butane–butene fraction requires 1.06 kg of caustic. However, this treatment does not remove the sulfur compounds completely. Ordinarily, up to 0.0155% mercaptan sulfur remains, and this is responsible for increased consumption of sulfuric acid in the alkylation process. For every kilogram of mercaptans entering the alkylation reactor, 52 kg of acid is reduced from a strength of 98% to 88%.

When the butane–butene fraction is demercaptanized with regeneration of the caustic, the caustic consumption is reduced to 0.06 kg/tonne, and the mercaptan content is reduced to 0.0005% by weight. In a typical alkylation unit with a capacity of 82,000 tonnes/yr, the saving of caustic amounts to $82{,}000(1.06 - 0.06)/1000 = 82$ tonnes/yr, and the saving of sulfuric acid $82{,}000(0.0155 - 0.0005) \times 52/100 = 650$ tonnes/yr.

In butane fractions that are to be used as feedstocks for dehydrogenation, the main organic sulfur compounds are also mercaptans; demercaptanization may be considered as fully justified. The same is true for isobutane fractions, which in the future will find increasing uses in dehydrogenation processes, thus imposing severe requirements on their content of mercaptan compounds.

In the demercaptanization of mixed butanes and mixed pentanes, various approaches are possible, depending on the processing scheme for gas separation. Thus, in order to reduce the consumption of caustic and improve the product quality, the demercaptanization of LPG can be applied across the board. With this approach, the content of sulfur in commercial LPG will be no greater than 0.002% by weight. It is virtually impossible to achieve this level of sulfur content by caustic treatment.

In Fig. 4 we show a flow plan for a unit used for the demercaptanization of a butane–butene cut at the Novo-Ufa refinery [16]. The fraction enters the column *1*, where it is treated with a countercurrent flow of amine to remove hydrogen sulfide. The fraction is further treated with caustic in column *2* to remove residual hydrogen sulfide. The hydrogen sulfide-free product, at a temperature of 15-35°C, is contacted for about 20 sec in column *3* with a countercurrent flow of catalyst complex in a 3/1 ratio (1/1 is better). The catalyst complex is prepared by dissolving 0.3-0.5 kg of cobalt polyphthalocyanine, periodically fed from tank *4*, in 1000 kg of a 10-20% caustic soda solution. In this stage of the treatment, the mercaptans are converted to mercaptides and pass into the caustic phase.

The mercaptan-free product passes into the settler *8* for separation of the caustic solution, and is taken off from the settler through a sand filter to the commercial product tank farm. The mercaptan-saturated catalyst complex is heated in an exchanger to 40-60°C and passes into the column *5*, to which air is fed for oxidative regeneration. The contact time between

TABLE 4

Organic sulfur compounds in C_5–C_6 fraction	Boiling point at 98 kPa, °C	Organic sulfur compounds in C_5–C_6 fraction	Boiling point at 98 kPa, °C
Before oxidation		*After oxidation*	
Methyl mercaptan	5,95	Dimethyl disulfide	109
Ethyl mercaptan	35,00	Diethyl disulfide	154
Isopropyl mercaptan	52,56	Diisopropyl disulfide	172,2
n-Propyl mercaptan	67,60	Dipropyl disulfide	180
tert-Butyl mercaptan	64,22	Di-*tert*-butyl disulfide	192
Isobutyl mercaptan	88,72	Diisobutyl disulfide	109*
n-Butyl mercaptan	98,46	Dibutyl disulfide	102^{2*}

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*At 0.173 kPa.

**At 0.146 kPa.

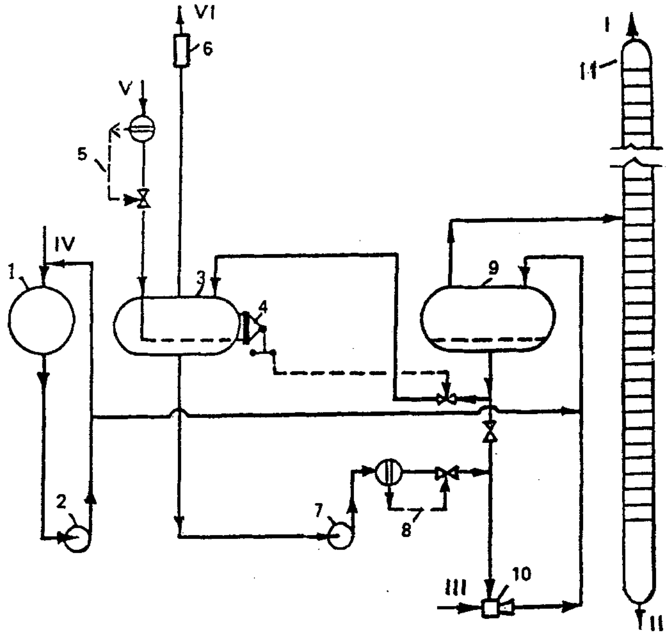

Fig. 5. Flow plan of unit for demercaptanization of pentanes: *1,3,9*) tanks; *2,7*) pumps; *4*) level controller; *5,8*) check valves; *6*) flame arrester; *10*) ejector-mixer; *11*) distillation column; *I*) treated pentane; *II*) residue with disulfides; *III*) feed; *IV*) caustic solution with catalyst; *V*) air for oxidation; *VI*) spent air to flare.

the catalyst complex and air is at least 5 min. From the regeneration column, the complex passes to the settler *6* for separation from the disulfides and is then pumped back to the system through a cooler, where it is cooled to 15-20°C. The disulfides are insoluble in the catalyst complex and are removed by simple settling.

A technologically attractive method for the removal of disulfides from light hydrocarbons is fractional distillation. The boiling point of disulfides is considerably higher than that of butanes and pentanes (Table 4). Therefore, disulfides can be readily separated from these hydrocarbons by distillation. From the caustic solution of catalyst, disulfides are extracted by the feed that is then separated in a distillation column into a mercaptan-free butane–butene or pentane–isopentane fraction and a residue representing a hydrocarbon fraction containing disulfides.

The residue from the treatment of pentanes is commonly used as a light component of gasoline. It always meets the standard for total sulfur content (no more than 0.1% by weight). Thus, the desired redistribution of sulfur-containing compounds through the fractions is achieved by a simple and ecologically clean method. This method can be readily implemented in existing units for gas separation at the same temperatures and pressures, without any additional formation of byproduct.

In Fig. 5 we show a flow plan for demercaptanization of pentanes at the Shkapovo gas processing plant [32]. Into a 5-10% aqueous caustic soda solution prepared in tank *1*, an aqueous solution of cobalt polyphthalocyanine is introduced at a temperature no higher than 40°C. After thorough mixing by circulation with the pump *2* and after analysis, the catalyst solution is pumped from tank *1* to tank *9*, from which, under a pressure above atmospheric, it is directed to tank *3*. From this tank, the solution is transferred by pump *7* through the check valve *8* to the inlet of an ejector–mixer, fed with a working fluid consisting of the feed – a medium-sulfur stabilized naphtha (C_5–C_6 fraction), cooled to 40°C or lower. The required ratio of input flows is maintained by means of flow controllers.

When the streams are mixed, mercaptans are extracted from the feed by the caustic solution to form mercaptides. The mixture passes to the tank *9*, where it separates into hydrocarbon and aqueous phases. The aqueous phase, a caustic solution of cobalt polyphthalocyanine containing sodium mercaptides, is directed to the tank *3* through a normally closed control valve *4* connected to a level indicator. For oxidation of mercaptans to disulfides, the product in tank *3* is sparged with compressed air fed through the check valve *5* and a manifold. The quantity of air input is controlled. The excess spent air from tank *3* passes through the flame arrester *6* to the flare system.

The emulsion of disulfides in caustic solution from tank *3* is fed by the pump *7* to an ejector–mixer for mixing with the feed. Upon mixing, the disulfides are extracted by the feed, and the mercaptans are extracted from the feed by the caustic solution. After layering of the mixture in tank *9*, the hydrocarbon phase – feed without mercaptans but with disulfides – passes into the distillation column. A mercaptan-free pentane–isopentane fraction is taken from the top of the column, and a still residue with disulfides is taken from the bottom.

Metal Polyphthalocyanines and Methods for Their Production

These compounds are characterized by the presence of paramagnetic centers; they are semiconductors, and they manifest catalytic activity in certain reactions [33]. Groups and bonds are repeated several times in their molecules, causing delocalization of valence electrons. With alternation of double and single bonds in polymers with a conjugation system, the clouds of *p*- (π-) electrons of all atoms entering into the molecule and forming double bonds will be set in a single plane and will overlap each other. As a result, a single collective system of delocalized and highly mobile π-electrons will be formed, covering the entire polyconjugation chain. Conjugation of bonds leads to a planar (coplanar) structure of the polymer molecule or to coplanarity of individual blocks of conjugated bonds (the blocks may be noncoplanar relative to each other).

Theoretical calculations have shown [34] that a coplanar system of conjugated bonds can include about 15 $C{=}C$ bonds (an idealized model of an isolated macromolecule). In real macromolecules, owing to steric hindrance, as well as the formation of crystalline regions and intermolecular interaction, the limiting length of conjugated sections will be shorter. Delocalization and collectivization of π-electrons, as well as complete or partial coplanarity of the macromolecule, are largely responsible for the semiconductor and catalytic properties of metal polyphthalocyanines.

In [35, 36], the catalytic activities of such polymers are compared with the number of paramagnetic centers in the molecule. In [37], a correlation was found between these parameters. The catalytic activity is also determined by the nature of the metal and addends entering into the chelate unit. These same factors are largely responsible for determining the selectivity of polychelated polymers with a conjugation system [38].

Cobalt polyphthalocyanine has a good system of conjugated bonds: The degree of polymerization is quite small (7-8), and hence the macromolecule is coplanar; also, the concentration of paramagnetic centers is greater than 10^{17} per gram of polymer [39]. In oxidation in the presence of cobalt polyphthalocyanine, molecular oxygen is activated, forming an ion radical $(O_2)^-$, which is highly reactive.

The highest catalytic activities are exhibited by metal polyphthalocyanines obtained under certain conditions from a mixture of pyromellitic acid or its derivatives (dianhydride or tetraanhydride), urea, a metal chloride or sulfate, and ammonium paramolybdate, which is used as a catalyst. Metal polyphthalocyanines obtained without the use of ammonium paramolybdate are lower in catalytic activity.

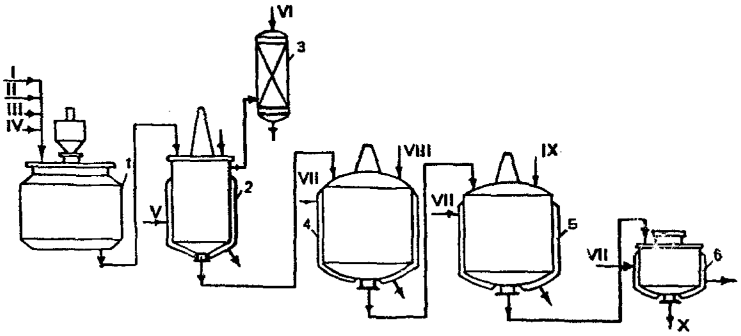

Fig. 6. Flow plan of unit for production of cobalt polyphthalocyanine: *1*) mixer for charge preparation; *2*) reactor; *3*) absorber; *4*) neutralizer; *5*) tank for alkalization; *6*) concentrating tank; *I*) pyromellitic dianhydride; *II*) urea; *III*) cobalt sulfate; *IV*) ammonium molybdate; *V*) ditolylmethane; *VI*) water; *VII*) steam; *VIII*) sulfuric acid; *IX*) sodium hydroxide; *X*) finished catalyst.

Depending on the mole ratio of components, the polymerization methods and conditions, and the methods used to purify the reaction products, metal polyphthalocyanines are obtained with molecular weights up to 5000 with an average degree of polymerization 5-8. The yield of the purified final product is 20-60% of the theoretical. The low molecular weight and low yields of metal polyphthalocyanines are explained by the fact that polymerization occurs mainly in the solid phase and that an infusible polymer is formed, so that the reaction is terminated in the seventh to eighth elementary act.

There is very little information to be found in patents or other published literature on the preparation of metal polyphthalocyanines as demercaptanization catalysts. As a rule, the firms that are involved do not publish information on the process technology. According to [12], metal polyphthalocyanines are obtained by fusing the dianhydride of pyromellitic acid with urea and metal salts at atmospheric pressure and temperatures of 170-200°C. The melt is heated with 16% hydrochloric acid and the solid phase is filtered off from the resulting suspension; the solid residue is dried, ground, and dissolved with heating in 96% sulfuric acid. Then the sulfuric acid solution is diluted with water, whereupon the metal polyphthalocyanines are precipitated, while the impurities remain in the solution. The precipitate is washed free of acid by decantation with water, filtered out, and heated at 40°C under high vacuum to remove the remaining impurities.

A number of studies have been devoted to the technology of obtaining cobalt polyphthalocyanine [40-42]. In [40, 41], it is obtained by melting tetracarboxylic acids or their dianhydrides with nitrogen-containing compounds, using ammonium paramolybdate as a catalyst. In [42, 43], it is proposed to obtain metal polyphthalocyanines by heating the tetranitrile of pyromellitic acid with metal salts at 120-200°C in ethylene glycol or dimethylformamide, without using any nitrogen-containing component.

Certain studies have been aimed at improving the methods of obtaining metal polyphthalocyanines. Particular attention has been given to increasing the yield of the desired product. In [44], it was proposed that pyromellitic dianhydride should be introduced into the composition of the mixture in the form of a complex with polycyclic aromatic hydrocarbons. The resulting metal polyphthalocyanine is freed of aromatic hydrocarbons by extraction with acetone. This method gives higher yields of metal polyphthalocyanines than can be obtained with the previously known methods. Thus, the yield of nickel, copper, and cobalt polyphthalocyanines are increased by 28, 16, and 20%, respectively. The method of preparing the mixture influences the yield and quality of the product. In [45] it is proposed that, before heating the mixture, the urea should be impregnated with an aqueous solution of ammonium molybdate (5-8% water relative to weight of urea), after which the metal salt and the pyromellitic dianhydride should be charged sequentially. As a result, the yield is increased by 5-12%, and the polyphthalocyanines of these metals are obtained with higher catalytic activities.

When using metal polyphthalocyanines as catalysts for demercaptanization, their stability is a very important factor. In caustic solutions in contact with oxygen, without any mercaptide ions, the phthalocyanines undergo gradual decomposition [46, 47]; the polymeric forms decompose at a higher rate than the monomeric forms. Metal polyphthalocyanines synthesized in the presence of a small quantity of certain monoanhydrides (such as phthalic anhydride) are characterized by higher stability [48, 49]. A method of synthesis proposed in [50] is of great interest for possible commercialization. Fusion of the mixture is performed in the presence of sulfuric acid (10-40% of the weight of the reaction mixture); a 1.0:1.4 mixture of pyromellitic

TABLE 5

Index	Okmer catalyst	
	Grade A (powder	Grade B (paste)
Content, wt. %, not greater than		
moisture	4	65–80
sodium hydroxide (relative to dry substance)	2	2
Catalyst activity: time required for conversion of at least 97% of mercaptan sulfur to disulfide, min, not greater than	4	4
Content of cobalt not bound into a complex, and determined in the form of mercaptide	None	

dianhydride and phthalic anhydride is used as the ligand-forming agent. Owing to the presence of sulfuric acid in the reaction zone, the volatilities of the reactants are reduced, and the yield of the desired product is increased. Metal polyphthalocyanines obtained by such a method embody the best properties of the polymeric forms (high activity) and the monomeric forms (good stability).

The commercial technology for obtaining cobalt polyphthalocyanine as a catalyst for the demercaptanization of petroleum products has been worked out by NIIneftekhim [All-Union Scientific-Research Institute of Petrochemical Production] [14]. The charge for obtaining cobalt polyphthalocyanine is prepared in a mixer (Fig. 6). Urea, ammonium molybdate, cobalt sulfate, and pyromellitic dianhydride, after drying and milling, are loaded into the mixer. After thorough mixing of the components, the prepared charge is unloaded into the reactor. Then the reactor charging hatch is closed, and the reactor heating system is turned on. The charge is heated by ditolylmethane circulated through the reactor jacket. The fusion temperature is 185-190°C, fusion time 6-8 h.

The gases and sublimate that are released during the fusion operation are taken off from the reactor to an absorber, where they are absorbed by circulating water. The line from the reactor to the gas absorber, and also the fittings, are steam-traced in order to prevent plugging with sublimate. The absorber is a packed column charged with Raschig rings and equipped with a jacket for cooling water. The circulating water, which contains ammonia, urea, and ammonium bicarbonate, is collected in a separate tank; after saturation, it is pumped to the wastewater treating section.

During the time of melting in the reactor, the nitrogen derivatives of pyromellitic dianhydride are cyclized, forming a porphyrin ring with conjugated bonds. Formed as an intermediate product is aminoiminoisoindolenine, which self-condenses to form chains of six to eight molecules. In the presence of metal salts, the four-unit chain is closed into a ring. Under optimal conditions, 70% of the pyromellitic dianhydride is consumed in the formation of cobalt polyphthalocyanine, and 30% is converted to the diimide of pyromellitic acid. In this reaction, the ammonium molybdate acts as a catalyst that becomes active at 150°C or higher through conversion to ammonium paramolybdate. Water and acidic products catalyze side reactions forming biuret and cyanuric acid from urea, leading to premature solidification of the melt and reduction of the cobalt polyphthalocyanine yield.

After the melting has been completed, hot water is fed to the reactor, and the melt is boiled for 2 h. The alkaline suspension of the melt that is formed in this operation is drawn off through the bottom valve of the reactor to a stirred neutralizer vessel. The operation of boiling is repeated until the melt is completely removed from the reactor.

The caustic-ammoniacal suspension of the melt is treated in the neutralizer with concentrated sulfuric acid to neutralize the ammonia solution and precipitate the cobalt polyphthalocyanine. The neutralizer is equipped with a steam jacket. To improve the precipitation of the cobalt polyphthalocyanine, a solution of polyacrylamide is added to the suspension. After it has settled, the upper aqueous layer is drawn off through a dip tube to a vacuum tank. The remaining material is washed to neutral reaction by the method indicated above.

The neutral suspension of cobalt polyphthalocyanine is taken off to a steam-jacketed stirred tank for alkalization. The calculated quantity of sodium hydroxide is fed to this same tank. The solutions of the suspension and caustic are mixed while heating at 100°C for 2-3 h. During this operation, the amide-imide cyclic functional groups of the cobalt polyphthalocyanine are hydrolyzed to carboxyl groups, with simultaneous neutralization of these groups by sodium hydroxide. At the end of the treatment, the cobalt polyphthalocyanine is obtained in the form of the sodium salt. The hot paste of sodium salt of cobalt polyphthalocyanine that is obtained in this tank is taken off through the bottom fitting to the concentrating tank, which is steam-jacketed. Water is driven off, down to the required residual moisture content in the final product – the catalyst. This operation can also be performed at 50-60°C with a residual pressure of 13.3-15.96 kPa.

The final product is used as a catalyst for demercaptanization under the name Okmer. This catalyst consists of the sodium salt of cobalt polyphthalocyanine with an admixture of sodium hydroxide. It is produced in the form of a violet-colored powder, and also in the form of a paste with a moisture content of 65-80%. The powdered catalyst is soluble in caustic solutions, poorly soluble in water, and insoluble in ether, acetone, and lower alcohols. It is classed as a low-toxicity compound: According to GOST 12.1.007–76, it corresponds to a Class 3 hazard. The maximum allowable concentration of catalyst dust in air in the workplace is 5 mg/m^3 (the same as for dusts that do not have any pronounced fibrogenic action) [51]. The permanent specification TU 38.1011134–87 has been developed for this catalyst. The specification requirements are listed in Table 5.

Important advantages of the Okmer catalyst are its high activity and the possibility of treating high-mercaptan feedstocks. The technoeconomic indexes of the demercaptanization process using this catalyst are at the same level as those of analogous foreign processes, and at a higher level for some of the indexes.

REFERENCES

1. S. G. Khabibullin, V. V. Fryazinov, M. L. Kreimer, et al., *Khim. Tekhnol. Topl. Masel*, No. 11, 14-21 (1987).
2. A. A. Gur'ev, T. I. Krivova, and I. Ya. Simanovskaya, in: *Chemistry of Organic Sulfur Compounds in Petroleum Crudes and Products* [in Russian], Vysshaya Shkola, Moscow (1968), Vol. 8.
3. A. M. Mazgarov, N. R. Vorob'ev, A. V. N'yaglov, et al., *Neftepererab. Neftekhim.*, No. 10, 25 (1975).
4. B. V. Losikov, *Petroleum Products: Properties, Quality, Application (Handbook)* [in Russian], Khimiya, Moscow (1966).
5. I. A. Rubinshtein, E. P. Sobolev, B. A. Énglin, et al., in: *Chemistry of Sulfur and Nitrogen Compounds in Petroleum Crudes and Products* [in Russian], BashFAN, Ufa (1960), Vol. 5.
6. E. P. Sobolev, E. S. Churshukov, I. V. Rozhkov, et al., *Khim. Tekhnol. Topl. Masel*, No. 9, 49-50 (1966).
7. N. I. Chernozhukov, *Technology of Oil and Gas Processing* [in Russian], Khimiya, Moscow (1978), Part 3.
8. K. M. Brown, W. K. T. Glein, and P. Urban, *Oil Gas J.*, **57**, No. 44, 73.
9. *Neft', Gaz Neftekhim. Rubezh.*, No. 4, 110 (1990).
10. USSR Inventor's Certificate 355,805.
11. USSR Inventor's Certificate 359,786.
12. USSR Inventor's Certificate 309,485.
13. E. P. Denisova, S. A. Borisenkova, T. A. Danilova, et al., in: *Catalytic Synthesis of Organic Sulfur Compounds* [in Russian], Sib. Otd. Akad. Nauk SSSR, Novosibirsk (1979).
14. R. M. Masagutov and A. Kh. Sharipov, in: *Summaries of Papers from Coordination Conference on the Review of Combined-Target Programs for the Growth of the Gas Industry* [in Russian], Baku, April 5-9, 1982; published by VNIPIgaz, Baku (1982).
15. A. M. Guseinov, Z. D. Seidov, Yu. V. Kirichenko, et al., *Neftepererab. Neftekhim.*, No. 5, 5-7 (1989).
16. R. I. Feizkhanov, R. Yu. Safin, P. G. Navalikhin, et al., *Neftepererab. Neftekhim.*, No. 10, 27-28 (1981).
17. USSR Inventor's Certificate 1,620,470.
18. G. A. Agaev, V. G. Kochetkov, and M. M. Mukhtarov, in: *Catalytic Synthesis of Organic Sulfur Compounds* [in Russian], Sib. Otd. Akad. Nauk SSSR, Novosibirsk (1979).
19. G. A. Agaev, V. G. Kochetkov, V. I. Khandzel', et al., in: *Summaries of Papers from All-Union Conference "Catalytic Methods for Exhaustive Desulfurization of Gases with Utilization of the Sulfur and Its Compounds"* [in Russian], Baku, May 7-10, 1980; published by VNIPIgaz, Baku (1980).
20. G. A. Agaev and V. S. Chernomyrdin, *Modern Methods for Treating Natural Gas to Remove Mercaptans* [in Russian], VNIIgazprom, Moscow (1981).
21. M. M. Mukhtarov, *Candidate's Dissertation,* Institute of Petrochemical Processes, Baku (1980).
22. USSR Inventor's Certificate 874,140.
23. A. M. Kuliev, G. A. Agaev, and V. G. Kochetkov, *Gazov. Promst.*, No. 2, 27-31 (1980).

24. B. D. Berezin and O. I. Koifman, *Usp. Khim.*, **49**, No. 12, 2389-2417 (1980).
25. S. A. Borisenkova, *Neftekhimiya*, **31**, No. 3, 391-409 (1991).
26. A. Kh. Sharipov, V. M. Kolychev, I. S. Faizrakhmanov, et al., in: *Summaries of Papers from 18th Conference on the Chemistry and Technology of Organic Compounds* [in Russian], Kazan, October 12-16, 1992; published by VNIIUS, Kazan (1992), Part 4.
27. K. M. Brown, R. R. Frame, and P. Urban, in: *The UOP Merox Process* (presented at UOP Technical Seminars), Moscow (1974).
28. R. M. Masagutov and A. Kh. Sharipov, in: *Catalytic Synthesis of Organic Sulfur Compounds* [in Russian], Sib. Otd. Akad. Nauk SSSR, Novosibirsk (1979).
29. K. M. Brown, *Commercial Results with the UOP Merox Process*, UOP, Des Plaines, Illinois (1969).
30. Z. D. Seidov, *Candidate's Dissertation*, Institute of Petrochemical Processes, Baku (1990).
31. A. M. Mazgarov, A. G. Akhmadullina, G. V. Tukov, et al., *Neftepererab. Neftekhim.*, No. 5, 28-30 (1975).
32. I. S. Faizrakhmanov, V. M. Kolychev, and M. A. Pais, in: *Summaries of Papers from All-Union Conference on the Technology and Pretreatment of Medium-Sulfur Gas Condensates and Crudes* [in Russian], Ufa, October 23-27, 1989; published by BashNII NP, Ufa (1989).
33. É. A. Silin', Ya. Ya. Ékmane, G. V. Khutareva, et al., *Vysokomol. Soedin.*, **10**, No. 8, 1786-1793 (1968).
34. V. V. Pen'kovskii, Yu. A. Kruglyak, et al., *Zh. Strukt. Khim.*, No. 10, 3-7 (1969).
35. I. R. Davydova, S. L. Kiperman, A. A. Slinkin, et al., *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 9, 1591-1598 (1964).
36. S. L. Kiperman and I. R. Davydova, *Kinet. Katal.*, No. 5, 762-772 (1961).
37. I. Dallard and T. Laedrich, *Bull. Soc. Chim. Fr.*, No. 12, 2204-2210 (1963).
38. N. P. Keier, G. K. Boreskov, V. V. Rode, et al., *Kinet. Katal.*, No. 4, 509-514 (1961).
39. A. A. Berlin, L. G. Cherkashina, and E. I. Balabanov, *Vysokomol. Soedin.*, **4**, No. 3, 376-382 (1962).
40. J. C. Bailar, *Wright Air Development Center, Technical Report* 57-35 (1958), pp. 657-661.
41. C. S. Marvel and J. H. Rossweiler, *J. Am. Chem. Soc.*, **80**, No. 11, 1197-1206 (1958).
42. E. Ger. Pat. 51,432.
43. A. A. Berlin, L. G. Cherkashin, and E. I. Balabanov, *Vysokomol. Soedin.*, **6**, No. 5, 832 (1964).
44. USSR Inventor's Certificate 602,221.
45. USSR Inventor's Certificate 1,620,126.
46. V. A. Fomin, A. M. Mazgarov, and N. N. Lebedev, *Neftekhimiya,* **18**, No. 2, 298-393 (1978).
47. A. F. Bil'danov, I. A. Arkhireeva, S. A. Gorokhova, et al., *Vestn. Mosk. Gos. Univ., Ser. 2, Khim.*, No. 6, 614-615 (1988).
48. R. J. Cotter and M. Matzner, *Ring-Forming Polymerizations, Part A, Carbocyclic and Organometallic Rings*, Academic Press, New York (1969).
49. A. A. Berlin, M. A. Geidrikh, B. É. Davydov, et al., *The Chemistry of Polyconjugated Systems* [in Russian], Khimiya, Moscow (1972).
50. USSR Inventor's Certificate 1,680,704.
51. Yu. A. Glukharev, É. R. Uzhdavshni, A. A. Mamaeva, et al., in: *Summaries of Papers from 3rd All-Union Conference on the Application of Polymeric Materials,* Kiev, April 3-6, 1981; published by Nauka, Kiev (1981).