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ECOLOGICALLY SAFE REAGENT RECYCLING OF CARBON BISULPHIDE OF THE HEAD FRACTION OF BY PRODUCT COKE INDUSTRIES

The paper considers technological peculiarities of extraction of head fraction of crude benzene at modern enterprises of by-product coke industry, the survey of existing methods of recycling of heat fraction and utilization of carbon bisulphide is carried out reagent method of carbon bisulphide extraction with formation of dialkyldithiocarbamine acides is suggested, their further possible practical application is considered.

Key words: *by-product coke industry, rectification, head fraction of crude benzene, carbon bisulphide additive.*

Introduction

Intensive gas effluents of metallurgy plants are one of the most actual problems in our country and in other industrial countries. By-product coke industry of Ukraine – is an integral part of metallurgy complex, one of the branches of heavy industry, that negatively influences the environment, since in the process of production considerable volumes of high toxic organic substances are formed. Besides, large volumes of coal dust are formed as a result of coal preparation before coking process. While coal cleaning by product coke plants more than 12 million/t of waste per year are formed. They contain considerable amount of coal.

Important aspect of environment protection in the process of operation of by-product coke plants is development of new processes and technologies, aimed at reduction of waste volumes and realization of wasteless coke production [1].

In the given paper we have analyzed available industrial methods of recycling of head fraction of crude benzene. These methods are rather material and energy-intensive, and the process itself – explosive and fire hazard; these methods are accompanied by considerable losses of carbon bisulphide (up to 30%) benzene, cyclopentadiene, the basic material for their obtaining is such non-renewable natural resource as coal. Entering the atmosphere, these substances cause damage to the environment due to their high toxicity [9].

The problem of rational, from ecological point of view, recycling of head (or carbon bisulphide) fraction of crude benzene and extraction of such toxic component as carbon bisulphate, by means of its chemical modification, with obtaining of valuable chemical products, that will find their further application in industry, remains very actual.

Formation of head fraction of crude benzene in the process of coke production

While high-temperature coking of charge in coke chamber volatile chemical products are formed along with coke, these products are complex inhomogeneous system, comprising gas and vapour-like substances – products of thermal decomposition of coal. Basic volatile products of high-temperature coking are: coke-oven gas, pyrogenetic moisture, naphthalene, ammoniac, hydrogen sulphide with other sulphur-containing compounds, cyanic compounds, aromatizing hydrocarbons (crude benzene), high-temperature coal resin, etc [1].

Fig. 1 shows simplified technological scheme of coking process, accompanied by formation of carbon bisulphide (head) fraction.

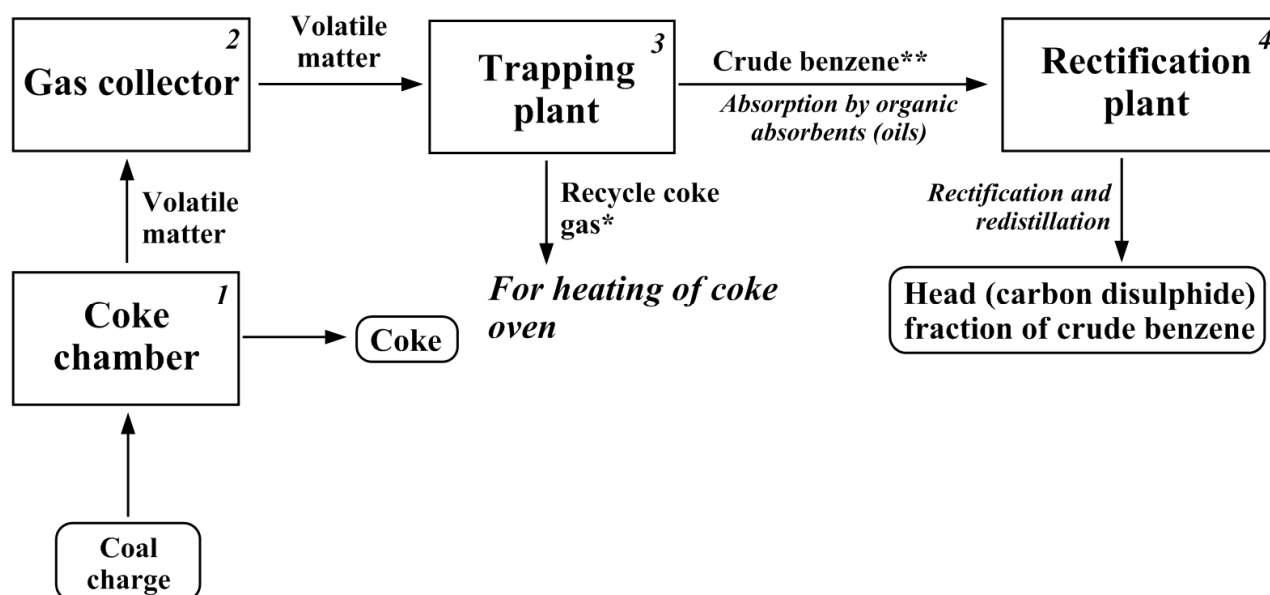


Fig. 1. Technological scheme of the process of head fraction of crude benzene formation

Notes: * – recycle coke gas is a mixture of H_2 , CH_4 , CO , CO_2 , N_2 , O_2 , remaining H_2S , aromatic and hydrocarbons of non-saturated series, minor quantity of nitrogen NO_x ;

** – crude benzene comprises benzene and its homologs (80 – 90 %) with admixture of non-saturated and sulphur-containing compounds, phenols, pyridine bases, etc..

Mixture of vapour and gas-like products of coking, arriving in gas collector form gas chambers, form so-called volatile matter. Content of volatile matter components is given in Table 1.

Table 1

Content of chemical products of volatile matter

Component	Concentration, l/m^3
Water vapours (pyrolysis and charge moisture)	250 – 450
Resin vapours	80 – 150
Aromatic hydrocarbons	30 – 40
Ammonia	8-13
Naphthalene	до 10
Hydrogen sulphide	6 – 40
Cianohydrogen	0,5 – 2,5

Besides the above-mentioned, volatile matter comprises carbon bisulphide (CS_2), carbon sulfoxide (COS), thiophene (C_4H_4S) and its homologues, light pyridine ($0,4 – 0,6 \frac{g}{m^3}$), phenols, etc.

Crude benzene, being multicomponent system, main components of which are single-nucleus, aromatic hydrocarbons and various admixtures, is eliminated from volatile matter by means of absorption of organic absorbents (oils).

Since crude benzene does not find practical application, it is subjected to further recycling in rectification plant in order to obtain, pure products. As admixtures, crude benzene contains unsaturated and sulphur-containing compounds, phenol, pyridine bases, etc. The number of various chemical compounds, crude benzene contains, is considerable. The content of greater part of these compounds is minor and in pure form they are not of practical value. Main volume of crude benzene is boiled away before the temperature reaches $180^\circ C$. Above this temperature low-boiling distillates of absorbing oil as well as unsaturated compounds, contained in crude benzene boil. All compounds, contained in crude benzene (distillate up to $180^\circ C$) conventionally are divided into five groups. Table 2 gives content and composition of these groups.

Table 2

Groups of compounds of low-building fraction of crude benzene

Group	Main compounds of the group	Content, %
Aromatic hydrocarbons	Benzene, toluol, dimethylbenzenes (xylons), ethylbenzene, trimethylbenzenes, ethyltoluols	80 – 95
Unsaturated compounds	Cyclopentadiene, styrol, kyramon, indene with homologues, cyclohexane, methye cyclohexane	5 – 15
Sulphur-containing compounds	Hydrogen sulphide, carbon bisulphide, thiophene, methylthiophene, dimethylthiophenes, trimethylthiophenes	0,2 – 2,0 (in terms of sulphur)
Saturated hydrocarbons of fatty and hydromatic series	Cyclopentane, methyl-cyclopentanes, cyclohexane, methylcyclohexanes, heptene, hexane	0,3 – 2,0
others	Phenol, nitrocompounds naphthalene	Less than 1,0

For purification of crude benzene and its fractions from unsaturated and sulphur-containing compounds, sulphuric acid purification and catalyst hydropurification are used in industry [1]. Independently on the chosen method of purification, carbon bisulphide fraction of crude benzene is extracted first, that contains resin-forming resources for production of polymer resins, allows to use carbon bisulphide fraction for obtaining carbon bisulphide and cyclopentadiene [2].

In modern practice of crude benzene recycling semicontinuous Hyprocoke technological scheme of separate recycling of two benzenes – the first and the second is widely used. According to this scheme continuous extraction of carbonbisulphide (head) fraction, pure benzene and toluol, periodic rectification of the residue, the second benzene and carbon bisulphide fraction is provided. To perform these tasks in rectification plants units of continuous and periodic action are available, these units consist of rectifying towers and condenser-cooling equipment, gauging tanks and collectors of process products.

Extraction of head fraction form the fist crude benzene is an important technological operation in all the schemes of crude benzene processing, including installation of hydropurification. Preliminary extracting of carbon bisulphide fraction allows to separate from benezene-toluol-xylol (BTX) fraction carbon bisulphide, that cannot be eliminated in the process of sulphuric acid purification, considerable amount of admixtures of saturated character as well as considerable amount of cyclopentadiene, that contributes to resin-formation in the process of sulphuric acid purification.

The amount of carbon bisulphid (head) farction, varying within 2 – 3 % from the fist benzene as well as the content, depends on conditions of rectification and the content of initial crude benzene [1]. Data of chromatographic control, presented in Table 3, show averaged composition of carbon bisulphide fraction of Jasinov by-product coke plant (Makeyevka).

Table 3

Physical characteristics and content of carbon bisulphide (head) fraction of Jasinov coke plant

Name of physical characteristics or component	Value
Density at 20 °C, $\frac{g}{cm^3}$	0,93 – 0,98
Distillation, °C:	
Start of boiling.....	30 – 38
Temperature of topping.....	60 – 75
Composition, %	
benzene.....	24,00 – 40,63
carbon bisulphide.....	17,29 – 28,75
thiophene.....	5,96 – 6,91
cyclopentadiene.....	5,48 – 12,98
dicyclopentadiene	1,55 – 15,91
hydrogen sulphide, saturated hydrocarbons, amylenes and other unsaturated compounds	10,12 – 30,42

Head fraction, formed by means of semicontinuous rectification of crude benzene, is colourless transparent liquid with unpleasant odour, in time it gets yellow colour due to oxidation of its components.

Recycling of carbon bisulphide fraction is carried out, applying the method of thermal polymerization, based on the property of cyclopentadiene to form dicyclopentadiene while heating, boiling temperature of which differs greatly from the temperatures of other components of the fraction. Dicyclopentadiene, being formed, is separated by means of further rectification.

In spite of the fact, that of all sulphur – containing compounds of crude benzene, only carbon bisulphate is of industrial value, if its content in carbon bisulphide fraction is small (less than 10 – 15 %), then the fraction is recycled only for extraction of dicyclopentadiene and benzene fraction [1].

Such method of recycling of crude benzene head fraction has a number of drawbacks: considerable time and energy losses, usage of cumbersome equipment, large losses of carbon bisulphide during the process

Another method of head fraction “utilization” is its non-rational and ecologically inadmissible burning as oven fuel at various industrial enterprises.

Physical-chemical and toxicological characteristics of carbon bisulphide

Along with thiophene and its homologues carbon bisulphide is main representative of sulphur-containing compounds in crude benzene. The content of these substances increases with the increase of cooking temperature. On condition of thorough rectification carbon bisulphide almost completely concentrates in head fraction [1].

Pure carbon bisulphide – is heavy ($1,29 \text{ g/cm}^3$) colourless liquid. Freshly distilled carbon bisulphide has ether smell, but while long storage the smell becomes to resemble the smell of turnip. Main physical chemical characteristics of this substance are given in Table 4 [3].

Table 4

Main physical chemical characteristics of pure carbon bisulphide

Denomination of the characteristics and unit of measurement	Value
Molecule CS_2 characteristic	
Structural formula.....	$\text{S}=\text{C}=\text{S}$
molar mass, g/M	76
Point of phase transition:	
Melting point, $^\circ\text{C}$	-111,61
Solidification temperature, $^\circ\text{C}$	-116,8
Boiling temperature, $^\circ\text{C}$	46,25
Thermodynamic and optic properties (at 20°C):	
Heat capacity c_p of liquid of carbon bisulphide, $\text{J}/(\text{kg}\cdot\text{K})$	1000
Evaporation heat at 0°C , J/g	374,7
Melting heat, J/g	57,78
Heat values of a combustion (liquid), kJ/M	1075
Refraction index for D-line of sodium ($\lambda = 589,3 \text{ nm}$).....	1,6276

Carbon bisulphide is used to produce cellulose xanthate for viscose manufacturing dithiodicarboxylic acids, for industrial syntheses of CCl_4 , as diluent extractant, vulcanizing agent for rubber and insecticide (due to its toxicity relatively the animals). In industry carbon bisulphide is produced by means of methane or natural gas reaction with the vapours of sulphur in presence of silica gel at temperature $500 - 700^\circ\text{C}$ in the chamber, made of chromium nickel steel. Carbon bisulphide of obtained by means of interaction of charcoal and vapours of sulphur at $750 - 1000^\circ\text{C}$, extracting it by distillation [8].

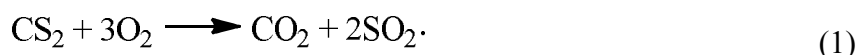
Independently on the method of carbon bisulphide extraction, its production is referred to very dangerous productions due to high toxicity of carbon bisulphide (permissible limiting concentration (PRC)) of carbon bisulphide vapours in industrial areas in different countries is form 1 to $10 - 60 \text{ mg/m}^3$, clethal dose of carbon bisulphide is 10 g/m^3 , as well as high fire hazard of carbon bisulphide,

having very low temperature of flash and self-ignition (236 °C), ability of carbon bisulphide to electrify, create explosions hazard mixtures with oxygen of the air in wide limits of concentrations. Carbon bisulphide vapour cause damage of nervous system and long work in the atmosphere with excess of carbon bisulphide PLC can lead to chronical poisonings, which become evident in different forms of nervous and mental disorders [3].

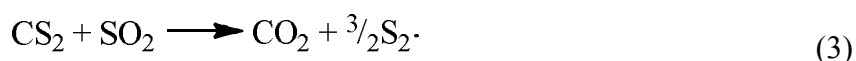
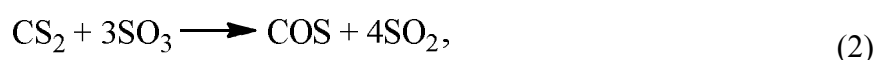
Methods of utilization of carbon bisulphide head fraction of coke production

As carbon bisulphide is very poisonous and easily ignites, its extraction from the head fraction in pure form is connected with fire and explosion hazards.

To render carbon bisulphide, containing in head fraction, harmless, its burning in the mixture with oven fuel is practiced:



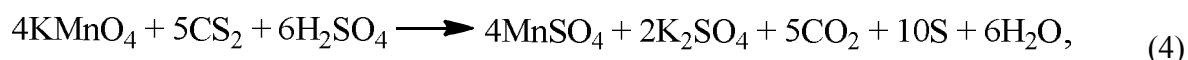
If the amount of oxygen is not sufficient, formation of CS, COS and sulphur vapour is possible, as well as side reactions may occur:



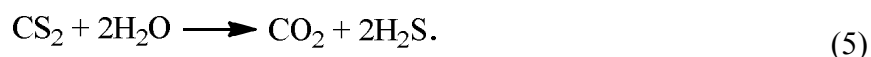
Thus, as a result carbon bisulphide burning large volume of high toxic compounds of sulphur is formed:

More suitable methods, enabling to render carbon bisulphide harmless, are the following

a) oxidation by potassium permanganate while heating with formation of two metals sulphates and elemental sulphur:



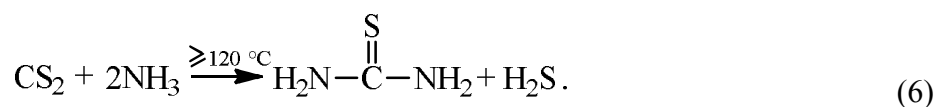
b) hydrolysis of carbon bisulphide by water vapour at temperature 400 – 450 °C:



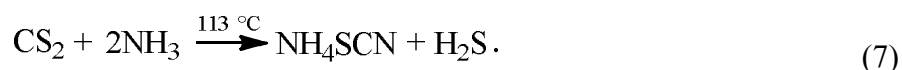
However, in this case high toxic hydrogen sulphide is formed [4].

Aqueous solution of ammonia was used as the reagent for extraction of carbon bisulphide from head fraction [5]. Ammonia is relatively cheap and accessible reagent, that can selectively interact with carbon bisulphide of the head fraction. Compounds, obtained while interaction of carbon bisulphide with ammonia, can be used for production of important and valuable products.

Depending on the temperature chemical nature of interaction process of carbon bisulphide with ammonia can be illustrated by the following reactions:



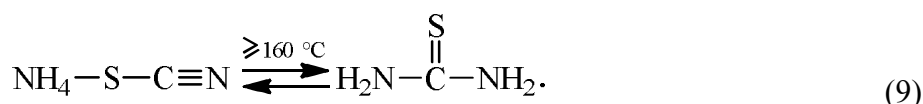
This and further chemical equations (7) are summing. One of the intermediate products of the reaction (6) is ammonia dithiocarbamate.



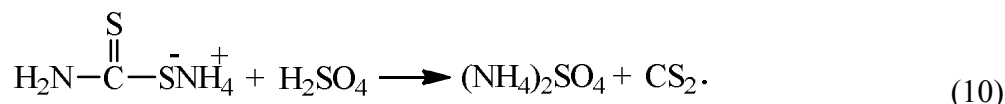
For bonding of liberating hydrogen sulphide the excess of ammonia is needed [9]:



Ammonia rhodanide is isomerized in thiocarbamide in accordance with the following scheme:



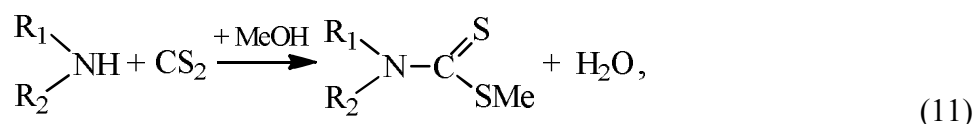
According to the above-mentioned reactions while interaction of carbon-bisulphide with ammonia we may obtain ammonia rhodanide, thiocarbamide, salts of dithiocarbamate acid. Acid decomposition of ammonia dithiocarbamate, being realized in conventional conditions, allows to regenerate carbon bisulphide.



Thus, it becomes possible to realize the technology of extraction of pure carbon bisulphide from the head friction in the form of prepared products [5]. However, in our opinion, this technology is rather difficult to realize in real (industrial) conditions.

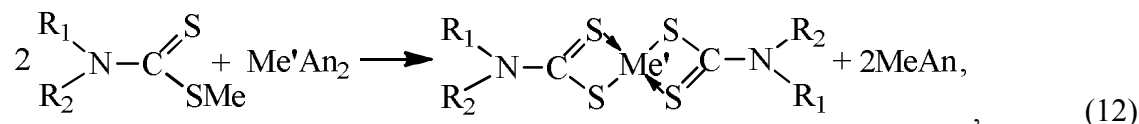
Utilization of carbon bisulphide by formation of metals dialkyldithiocarbamates

Taking into account that emission of carbon bisulphide is of great ecological hazard, two stage (single-reactor) technology of carbon bisulphid utilization in the composition of carbon bisulphid fraction was developed, this technology includes formation of N,N salts of dialkyldithiocarbamate acid from carbon bisulphide fraction without extraction or concentration of the latter - [6 – 7]:



where

$\text{R}_1 = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$; $\text{R}_2 = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$, $\text{Me} = \text{K}^+, \text{Na}^+, \text{NH}_4^+, \text{R}_1\text{NH}_3^+$ with their further transformation into corresponding N,N-diakyldithiocarbamates of certain s-, p- and d-metals using the scheme:



where $\text{Me}' = \text{Cu}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Sn}^{2+}, \text{Pb}^{2+}, \text{Hg}^{2+}, \text{Cd}^{2+}, \text{Mg}^{2+}, \text{Ba}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}$;

$\text{An} = \text{Cl}^-, \text{NO}_3^-, \frac{1}{2}\text{SO}_4^{2-}$.

Physical chemical characteristics of the obtained compounds are given in Table 5, 6.

Table 5

Physical-chemical characteristics of dialkyldithiocarbamates of general formula $\text{R}^1\text{R}^2\text{NC}(=\text{S})\text{SMe}$

№ comp	Substitutes		Cation Me^+	Mol. mass	Gross-formula	$T_{\text{ml}}, ^\circ\text{C}$	output, %
1	CH_3	CH_3	Na	143	$\text{C}_3\text{H}_6\text{S}_2\text{NNa}$	438*	85
2	C_2H_5	C_2H_5	Na	171	$\text{C}_5\text{H}_{10}\text{S}_2\text{NNa}$	93-95	81
3	C_3H_7	C_3H_7	Na	199	$\text{C}_7\text{H}_{14}\text{S}_2\text{NNa}$	54-59	95
4	C_4H_9	C_4H_9	Na	227	$\text{C}_9\text{H}_{18}\text{S}_2\text{NNa}$	39-40	92
5	C_2H_5	H	$\text{C}_2\text{H}_5\text{NH}_3$	166	$\text{C}_5\text{H}_{14}\text{S}_2\text{N}_2$	38-42	90

Note: * – self-ignition temperature.

Table 6

Physical-chemical characteristics of N,N- dialkyldithiocarbamates of general formula Me'L₂*

Groups of metals relatively the position in PS**	General formula metal Chelate	Gross-formula	Output %	T _{ml} (decomposition), °C	Colour of the compound	Mol. mass	Calculated, %		Found, %	
							N	Me'	N	Me'
1	2	3	4	5	6	7	8	9	10	11
s- metals	MgL ₂	C ₆ H ₁₂ N ₂ S ₄ Mg	41,8	> 260	white	264	10,58	9,18	10,06	8,95
	CaL ₂	C ₆ H ₁₂ N ₂ S ₄ Ca	40,3	> 300	white	280	9,99	14,29	9,58	14,07
	SrL ₂	C ₆ H ₁₂ N ₂ S ₄ Sr	35,6	> 310	white	328	8,54	26,71	8,17	26,20
	BaL ₂	C ₆ H ₁₂ N ₂ S ₄ Ba	36,4	> 280	white	377	7,42	36,35	7,14	36,02
p- metals	SnL ₂	C ₆ H ₁₂ N ₂ S ₄ Sn	85,3	152 – 160	yellow	359	7,80	33,06	7,34	32,91
	PbL ₂	C ₆ H ₁₂ N ₂ S ₄ Pb	72,6	170 – 180	light-grey	447	6,26	46,29	5,88	45,81
d- metals	CuL ₂	C ₆ H ₁₂ N ₂ S ₄ Cu	95,4	185 – 200	brown	304	9,22	20,91	8,89	20,54
	ZnL ₂	C ₆ H ₁₂ N ₂ S ₄ Zn	88,8	254 – 257	white	305	9,16	21,38	8,66	21,27
	CdL ₂	C ₆ H ₁₂ N ₂ S ₄ Cd	83,9	> 325	light - yellow	352	7,94	31,86	7,43	31,48
	HgL ₂	C ₆ H ₁₂ N ₂ S ₄ Hg	76,9	160 – 171	grey	441	6,35	45,48	6,02	44,95
	MnL ₂	C ₆ H ₁₂ N ₂ S ₄ Mn	82,8	175 – 190	yellow - grey	295	9,49	18,60	9,09	18,14
	FeL ₂	C ₆ H ₁₂ N ₂ S ₄ Fe	92,4	175 – 180	black	296	9,46	18,85	8,97	18,37
	CoL ₂	C ₆ H ₁₂ N ₂ S ₄ Co	83,5	260 – 275	green	299	9,36	19,69	9,24	19,20
NiL ₂	C ₆ H ₁₂ N ₂ S ₄ Ni	96,2	270 – 285	light- green	299	9,37	19,62	9,03	19,25	

Note: * – symbol of organic ligand L: (CH₃)₂NC(=S)S⁻;

** – abbreviation: PC – Periodic system of chemical elements.

Practical application of the obtained products of chemical bonding of carbon bisulphide

It was established that dialkyldithiocarbamates are used as additives to industrial oils, they possess antiwear, antisciriong, antioxidant and anticorrosive properties, due to simultaneous presence in the structures of such elements as Sulphur and Nitrogen. Combined presence of these elements provides oils better antioxidant and anticorrosive properties, as compared with compounds, separately containg Sulphur or Nitrogen.

Dialkyldithiocarbamates of metals of general formula [R¹R²NC(=S)S]_nMe', де Alk: R₁ = R₂, R₁ ≠ R₂, heterocyclic radical; Me' = Zn, Cd, Ni, Co, As, Bi, Sb, Se, Ba, Mg; x = 2, 3, due to its high anticorrosive properties is widely used in motor oils, operating at high temperatures.

Additive Vanlub-61 (Vanlub-AZ) is the example of practical application of such compounds, this additive consists of 50% mass of dialkyldithiocarbamates metals (Cd, Zn) in motor oil, another additive S-6852 – is barium dialkyldithiocarbamate [10].

Other scientists propose to use as anticorrosive additives to oils dithiocarbamates of the common formula R¹R²NC(=S)S R³, where R₁ = R₂ = alkyl, cycloalkyl, aryl or hydroxyl-containing hydrocarbon radicals, saturated and unsaturated N,O-containing heterocyclic radicals; R₃ polybutene radical with average molecular mass less than 1500 [11].

Dithiocarbamates also possess valuable analytical properties enabling to use them as the reagents for various purpose and high reaction ability and relative simplicity of syntheses provides their wide usage in organic synthesis, flotation while concentration, rubber vulcanization, in medium and biology as protectors of radiation protection (dithiocarbamates of rare-earth metals) as well as basic compounds while synthesis of chemical means of plants protection [12].

Conclusions

1. Technological peculiarities of crude benzene head fraction extraction at coke producing enterprises are considered, composition and physical chemical characteristics of crude benzene head fraction, containing high toxic carbon bisulphide are given.

2. The survey of main methods of head fraction recycling and utilization of carbon bisulphide is

carried out, their advantages and drawbacks are shown.

3. Reagent method of carbon bisulphide extraction with formation of N, N dialkyldithiocarbamates.

4. The possibility of practical usage of mettalic salts and derivatives of dithocarboxylic acids in various branches of industrial production is considered.

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