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Association of independent consultants
in mineral resources, metallurgy and chemical industry

Anthracene Oil Market Research in the CIS

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ANNOTATION

The report is devoted to investigation of current standing of market of anthracene oil in the CIS and forecast of its development. The report is composed of 4 Sections, contains 38 Pages, including 7 Figures, 8 Tables and Appendix.

Methodologically, the work was implemented in 2 stages – "desk" studies and "field" activity by telephone interview method. At the first stage, we analysed many information sources, first of all, data of state bodies: Federal Service of State Statistics of Russia (Rosstat, FSSS of Russia), State Committees on Statistics of CIS countries, Federal Customs Service of Russia (FCS of Russia), State Customs Committee of Ukraine (SCC of Ukraine), official domestic railage statistic of JSC RZhD (former Ministry of Railway Transport of Russia), sectoral (industrial) and regional press, annual and quarterly reports of companies, data from web-sites of company-producers, as well as own InfoMine database.

At the second stage, the summarized and analysed data were verified and corrected by the way of telephone interviews with specialists of Russian and Ukrainian companies, described and mentioned in the report.

The first Section of the report presents information on methods of obtaining anthracene oil and resources used, describes directions and volumes of supplies of the resources to anthracene oil producers.

The second Section is devoted to analysis of production of anthracene oil for 2003-2008, including description of current standing of its producers, data of resources base, volumes of the production, plans on development of the company-producers, as well as data on volumes and directions of supplies of anthracene oil in latest years.

The third Section describes consumption of anthracene oil and presents review of key end-uses of the product.

The fourth Section of the report gives forecast of development of anthracene oil market.

The Appendix presents addresses and contact information on companies, involved in production and consumption of anthracene oil.

INTRODUCTION

Anthracene oil is a heavy yellowish-green coal-tar fraction (partially solidifying on cooling), which distills over from coal tar at a temperature above 270° (up to 400°C); its density is 1.09-1.10 g/cm^3. It is a complex mix of high-boiling aromatic (and other) compounds, basic of which are anthracene (around 5%), phenanthrene (around 20%), and carbazole (6%). The oil is the principal source of anthracene. When cooling anthracene oil, soft mass originates, basic part of which is anthracene.

Anthracene oil is used as a source of anthracene, phenanthrene, and carbazole, as well as in production of carbon black. Anthracene oil is one of the best antiseptic agent for protecting wood and is so used for preparing sleeper-impregnating oil. Besides, it is used in electrode industry as additive to pitch (1-3%), when decreasing temperature of pitch softening is required for facilitating filling case with electrode mass.

Anthracene oil has sharp wicked odour. Permissible level of antracene (the most toxic component of the oil) content in working zone air is 0.1 mg/m^3. Unlike other polycyclic aromatic hydrocarbons, anthracene is not carcinogenic but has been recently included in the Substances of Very High Concern list (SVHC) by the European Chemicals Agency (ECHA) because being considered Persistent, Bioaccumulative and Toxic (PBT) for freshwater and marine ecosystems within the REACH framework.

Operations with anthracene oil requires strict sticking safety instructions and fire-prevention rules. Workers must have special cloth and protecting glasses. Uncovered parts of body must be protected with special protecting pastes, containing starch, glycerin, gelatin and other components.

Flash point of anthracene oil − 141°C.

Firing point − 171°C.

Self-ignition point − 548 °C.

Temperature interval of firing anthracene oil vapor: bottom − 120°C, upper − 160°C.

I. Process of production of anthracene oil and resources used

I.1. Obtaining anthracene oil in the course of processing of coal tar

In industry anthracene oil is obtained from ***coal tar***.

Coal tars are by-products of the carbonization of coal to produce metallurgical coke and/or natural gas. Annual global production of 400 mln t of coke is accompanied by obtaining around 16 mln t of coal tar. Notice that some coke shops (in USA, China) apply process, which doesn't provide further processing of coal tar, which is simply burnt in the process of coke production, From estimates, only around 50% of coal tar, produced in the world, are subjected to further processing to obtain additional commodity products.

Coal tar is a product of the destructive distillation of bituminous coal, when coal tar is mainly generated in the course of pyrogenetic decomposition of primary tar in coking process.

Coal is converted to coke in large coke oven batteries. The coking process consists of heating crushed coal above 900ºC in the absence of air to drive off the volatile compounds; the resulting coke is a hard, but porous carbon material that is used for reducing the iron in the blast furnace. The modern by-product coke oven recovers volatile chemicals in the form of coke oven gas, tars, and oils.

Tar is released in the course of the whole coking process: initially, primary tar is released, containing mainly aliphatic compounds. With increasing temperature, formation of aromatic hydrocarbons begins. Further heating results in formation of polycyclic compounds. For instance, maximal generation of naphthalene and anthracene is reached at 1000ºC.

Coal tar is a product of thermal breakdown of primary tar. The bulk of primary products (90-95%) raises to near-roof space of oven, where it is mixed with released gases, heated and the first stage of decomposition proceeds, with the primary products conversion into high-temperature tar, benzene and other products.

Releasing of coal tar from coking gas proceeds by several stages: the first stage – when cooling the coking gas in gas collector by over-tar water from 750˚C to 80˚C, and the second – when cooling coking gas in primary gas coolers.

Coal tar is obtained in by-product recovery shops of by-product coke enterprises. The obtained tar is mixed and goes to further processing.

Composition, yield and properties of coal tar depend on composition of charge, design of ovens and coking conditions (first of all, on temperature of near-roof space of oven and period of aging volatile components in the oven). At by-product coke enterprises of CIS, yield of coal tar in per cents of metallurgical coke ranges 4.0-4.9%.

Coal tar is a brown or black liquid of high viscosity, which smells of naphthalene and aromatic hydrocarbons. Quality of coal tar is characterized by density, yield of fractions, content of phenols, naphthalene, as well as toluene-insoluble compounds, moisture. Density of coal tar ranges 1120–1220 kg/m3, being one of the most important properties, characterizing quality of coal tar and its fractions. Density of coal tar is determined, to a large extent, by content of compounds, insoluble in toluene or xylene – increasing share of the compounds owes

raising the density and decreasing yield of oils and phenols in the course of its processing.

Coal tars are complex and variable mixtures of polycyclic aromatic hydrocarbons (PAHs), phenols, heterocyclic oxygen, sulfur, and nitrogen compounds. In chemical properties, all the components of coal tar are subdivided into 3 groups: neutral, acid and basic.

The neutral hydrocarbon compounds are mainly presented by *napthalene* $C_{10}H_8$, *anthracene* $C_{14}H_{10}$, *chrysene* $C_{18}H_{12}$, accompanied by indole, carbazole, benzo-carbazole, styrene, indene, cumarole and their derivatives.

Sulfur-containing neutral compounds of coal tar are presented by *thiophene* C_4H_4S, thionaphthene C_8H_6S (and their methylated derivatives), di-phenyl sulfide, an-benzo-thionaphthene and other. Most of the compounds occurs in washing (absorption), napthalene and anthracene fractions. However, their separation in the course of fractionation (rectification) is not possible owing to closeness of their boiling points to those of hydrocarbons. Most of the sulfur-containing neutral compounds is harmful impurity in products of coal tar processing – distillation and so are removed from distillates (fractions, technical products) by chemical purification and other methods. The most hard-removable compound is thionaphthene.

Summarized content of the neutral compounds in coal tar reaches 42–43%. The most valuable of them are napthalene and anthracene, which are distilled from coal tar in napthalene and anthracene fractions, respectively.

Acid part of coal tar is presented by compounds, containing oxygen in side chain: *phenol* C_6H_5OH, *cresols* $C_6H_4CH_3OH$, *xylenols* $C_6H_3(CH_3)_2OH$ and polycyclic phenols, total content of which reaches 1.2–2.0%. The most valuable components are phenol and *o-, n-, м-cresols*. Most of the compounds is distilled from coal tar in phenol fraction, and the rest is spread over other fractions. Phenols from fractions are separated by their treating with alkaline solutions to obtain phenolate.

Basic properties are demonstrated by *nitrogen-containing compounds* of coal tar – *pyridine* (C_5H_5N), *xynolene* (C_5H_7N) and their derivatives, as well as high-boiling bases. Total content of bases in coal tar reaches 0.8–1.2%. In the course of distillation of coal tar the compounds are spread over fractions depending on boiling point. Separation of bases from fractions and oils is conducted by treating with sulfuric acid.

Coal tar is processed in tar-processing shops of by-product coke enterprises; there are 16 such shops in the CIS territory now.

Processing of coal tar includes the following main stages:

- preparation of coal tar for processing;
- final dewatering;
- rectification (distillation) to obtain fractions (distillates);
- processing of fractions;
- chemical purification of fractions and oils from phenols and pyridine bases;
- treating of mid-temperature pitch;
- obtaining high-temperature pitch and its coking;
- obtaining purified naphthalene, anthracene and other products.

Coal tar from by-product recovery shops arrives by pipeline to a surface storage (reservoir) of tar storehouse. To tar-processing shops, coal tar arrives at moisture up to

4% and ash content up to 0.1%. Such coal tar requires purification from water, dissolved salts and ash. The tar storages provide stability of tar composition and its partial dewatering, desalting and ash removal.

The storehouse includes at least 4 reservoirs (both underground and surface), positioned in cascade order, as well as water and oil collectors. The surface storages are individual reservoirs with capacity up to 3000 m^3, equipped with bottom heaters for heating coal tar up to 70–80°C. Top part of each reservoir includes collector for periodical self-discharge of over-tar water.

Tar-processing shop at enterprises of CIS use practically a single flow chart, providing for distillation of coal tar at its one-time evaporation in continuous tube facility, equipped with one or two rectification columns. Most of large enterprises has design capacity on coal tar processing shop of 200 kt of coal tar per year. Depending on rectification apparatus and operating practice, specific quantitative yield of fractions and their various qualities are obtained.

Unlike rectifying crude benzene, conducted by successive evaporation of its individual components, in rectifying coal tar, one-time evaporation and fractional condensation principle is applied.

At the first stage of processing of coal tar in tube facilities, one-time evaporation of coal tar is conducted, determining yield and composition of resulted vapor and liquid phases, degree and quality of transfer of individual components of coal tar into fractions. The evaporation provides quick heating of coal tar in heat coils, from which coal tar goes to evaporator, in which, as a result of sharp pressure release, vapors are immediately separated from liquid, forming distillate. At the second stage, the obtained distillate is rectified in rectification column to separate it into narrow fractions depending on their boiling points. Initially, in the column bottom, high-boiling fractions are condensed – anthracene, then washing, napthalene, phenol, which are removed as liquids by side bleeding. Light fraction is taken from the column top as vapor.

The tube heating coal tar – processing facilities are characterized by a number of important advantages, including:

high producibility and compactness;

low area of the facility;

stability of mode and reduced period of thermal action on coal tar, resulting in increasing yield of fractions;

high controllability of the process;

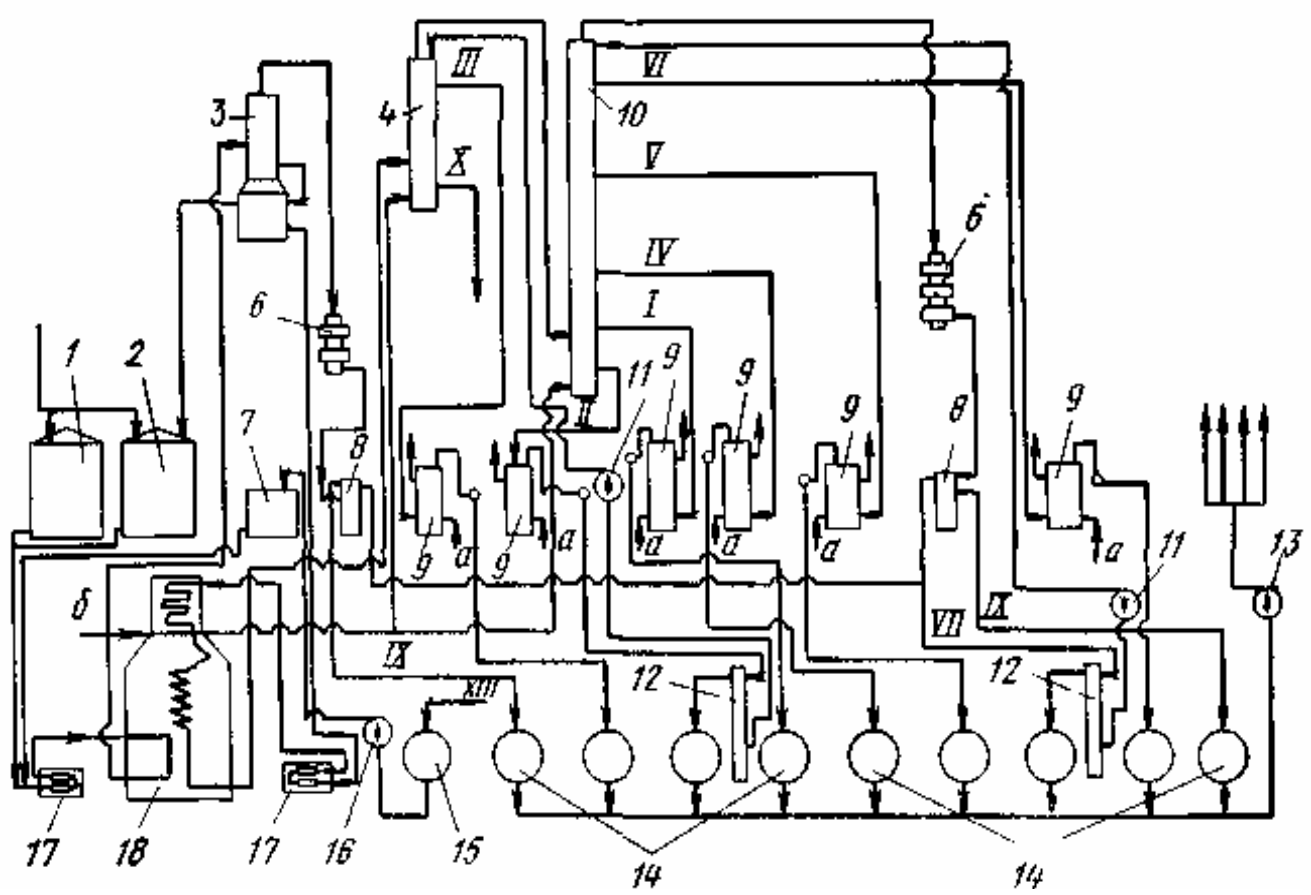
low risk of fire (compared with periodic-type facilities).

In two-column tube facilities, heating of coal tar up to one-time evaporation temperature is conducted in radiant-convection chamber-type tube furnaces with productivity of 100–200 kt of coal tar per year. Distillate formation and its rectification is conducted in pitch (anthracene) and fractioning columns.

At present time, the most widespread is one-column tar-rectification facility (Fig.1). The facility is equipped with tube furnace with productivity of 200 kt of coal tar per year with heating walls, containing flame-free panel burners of system «Giproneftemash» and two-side lighting shield. The rectification column, compared with the fractioning column of two-column facilities, has more plates for distillate

division into 5 liquid fractions and light oil vapor. This scheme allows to obtain 3 anthracene fractions. Change to one-column facilities allowed to simplify apparatus arrangement of facilities and to improve rectification of evaporated part of coal tar.

Figure 1: Coal tar rectification flow sheet in one-column tube rectifier



I, II, III – anthracene fractions; *IV* – washing (absorption) fraction; *V* – napthalene fraction; *VI* – phenol fraction; *VII* – light oil; *VIII* – soda solution; *IX* – ammonia aqua; X – pitch; *а* – cooling water; *б* – super-heated steam

1, 2 – storing reservoirs; *3* – 1st stage evaporator; *4* – 2nd stage evaporator; *6* – condenser-cooler; *7* – mixer; *8* – separator; *9* – cooler; *10* – rectification columns; *11, 13, 17* – pumps; *12* – reflux tank; *14*, *15* – collectors; *18* – tube furnace

Source: review of scientific and technical literature

Simplified flow sheet of coal tar processing to obtain various fractions is presented in Fig. 2.