

plexon concentration was changed were carried out. The obtained data are presented in figure 3. It is seen from this figure that at OMED concentration equal to 4...8 mg/l corrosion rate has the smallest values. Therefore these concentrations may be taken as operating ones.

The influence of two component inhibitor OMED – zinc sulfate on fouling in aqueous environments

Besides corrosion decrease and prevention of hardness salt deposits, the important property of any inhibitor is an ability to suppress vital activity of animalcular organisms, developing in aqueous environments and forming the great bulk of fouling on heat exchanging surfaces. Therefore, after weighing the samples of stain-

less steel, from their surface smears were taken, put on a slide and visually examined under a microscope. The results of investigations showed that two component inhibitor OMED – zinc sulfate does not stimulate fouling processes in aqueous environment.

Thus, the results of investigations, carried out in laboratory environment, indicate the composition of organophosphorous complexon OMED (salt of 1-ox-ethylidene-diphosphonic acid with 2-dimethyl-amino-methylphenol) and zinc-sulfate being the effective inhibitor of corrosion and salt precipitate in aqueous environment. Therefore it may be applied for two-bath process of circulating water in systems of recycling cooling of industrial enterprises.

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HIGH-BOILING COMPONENTS IN STRAW OIL

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Investigation of straw oil and polymer quality produced in the process of its regeneration has been carried out. The conclusions about using polymers as a material for base end products are made. Flow scheme of technological treatment of straw oil wastes is suggested.

In the process of coal coking considerable quantity of resin is generated which contains in its composition enormous quantity of organic compounds the large amount of which is difficult to be obtained in other technological processes. Such condensed compounds as acenaphthene, dibenzofuran, fluorene and others are in resin in quantities more than 1 % (per resin). At the same time there is a real requirement for these compounds as raw materials in different branches of applied chemistry and pharmaceutical chemistry.

The technology of coal-tar resin reprocessing at domestic enterprises of by-product-coking industry is mainly carried out at single-column rectification devices with target fraction selection according to column height. Stripping fraction is usually selected from the

17th tray. More than 140 individual compounds are in its composition [1]. The greater bulk is presented by 23 components of aromatic series with boiling temperatures 218...293 °C. Moreover, about 40 nitrogenated compounds and 16 components of phenolic series are in the fraction. Quality of straw oil is determined by absorbing capacity (quantity of methylnaphthalenes), tendency to crystallization when cooling and tendency to polymerization at high temperatures, for which high-boiling components: acenaphthene, diphenylene dioxide, fluorene are responsible [2–4].

High-boiling compounds emission by means of additional rectification of straw oil solves the problem of both straw oil quality improvement and raw materials for emission of individual high-boiling components. In

a flowsheet of a benzene department of a modern by-product coke plant this problem is solved by a straw oil regenerator: while regenerating, oil quality is improved and polymers in which the considerable part of high-boiling compounds is concentrated are removed.

Straw oil regeneration is carried out from time to time as polymers are accumulated in reverse oil and its density increase.

The results of straw oil quality research are presented below. Polymers characteristics at the beginning and at the end of regeneration cycle are also given. Main oil quality indexes are density and breakup. Density is the most prime and operating characteristic permitting for control of straw oil condition. Temperatures of breakup characterize content of naphthalene fraction residuals to 230 °C; content of components responsible for oil absorbing capacity to 230...270 °C; content of high-boiling components – acenaphthene, diphenylene dioxide, fluorene to 270...300 °C.

Table 1. Quality of straw oil and polymers

№№	Density, kg/m³	Water, %	Breakup, %			270...300 °C
			230 °C	270 °C	300 °C	
Raw straw oil						
1	1059	0,4 0,3 0,3 0,8	1,6	79,0	85,0	6,0
2	1059		2,4	88,0	92,0	4,0
3	1056		1,4	84,0	88,0	4,0
4	1059		0,9	87,0	93,0	6,0
Reverse oil						
5	1066	0,1	0	76,0	92,0	16,0
6	1064	0,1	1,0	82,0	93,0	11,0
7	1076	0,1	0,4	79,0	91,0	12,0
8	1063	0,2	2,5	81,0	89,0	8,0
9	1059	0,2	1,7	82,0	90,0	8,0
Refiltered oil						
10	1055	0,1	0,8	80,0	93,0	13,0
11	1053	10,4	1,8	80,0	90,0	10,0
12	1056	2,0	0,6	86,0	95,0	9,0
13	1049	1,6	7,9	85,0	91,0	6,0
Polymers						
14	1138	–	0,5	21,0	75,0	54,0
15	1144	–	1,0	21,0	72,0	51,0
16	1105	–	1,2	52,0	82,0	30,0
17	1105	1,2	1,4	45,0	74,0	29,0
18	1100	0,1	0,2	56,0	78,0	22,0

Oil and polymers breakup is determined by distillation in Wurtz bulb at temperature checking at yield of boiling mixture vapor phase. It might be supposed that the main quantity of high-boiling components presenting in oil is removed at distillation in the temperature range 270...300 °C.

In raw straw oil quantity of the product boiling away in the range 270...300 °C (1–4, table) is 4...6 % (by mass).

In reverse (experiment 5–9) and refiltered oil (10–13) high-boiling fraction yield is nearly twice as high as raw straw oil. In a polymer this fraction yield reaches 50 %.

Noted decrease of 270...300 °C fraction yield to 30 % and lower (pos. 16–18) is accounted for cyclic carrying out of regeneration process: experiments 14–15 are referred to the beginning of the cycle and 16–18 on-

es are referred to the end of this cycle which lasts approximately 8–10 days.

In the process of trapping and distillation of benzene hydrocarbons resin straw oil undergoes the series of changes: it is compacted, loses the considerable part of light distillates, temperature of crystallization rises.

Series of factors depending on oil composition, content of elements in coke oven gas promoting its sealing, oil application conditions in technological system influence the rate of polymerization of resin oil components. Instability of resin straw oil fractions increases at total magnification of a part of polynuclear aromatic compounds having greater reactivity and tendency to compacting than mononuclear and bicyclic structures.

Fractions with boiling temperature 280...285 and 285...295 °C are polymerized most intensively. Density and viscosity of these fractions increases considerably that decreases oil quality on the whole [5].

Fractions boiling away to 270 °C are the most resistant to polymerization that improves technological properties of straw oil and allows decreasing its discharge intensity. Chromatographic analysis of straw oil from different parts of flowsheet and also polymers has been carried out.

The content of high-boiling components: acenaphthene, diphenylene dioxide, fluorene (table 2) is of greatest interest.

Table 2. Content of high-boiling components in straw oil and polymers

№	Acenaphthene	Diphenylene dioxide	Fluorene	Anthracene+phenanthrene	Σ HBC
Raw straw oil					
1	20,05	11,32	7,09	0,06	38,71
2	20,37	11,20	6,42	0,05	38,04
3	19,25	10,90	6,23	0,08	36,46
4	18,68	10,53	5,93	0,09	35,22
Reverse oil					
5	22,28	14,90	7,66	0,41	47,25
6	24,85	15,78	6,85	0,17	47,64
7	30,09	16,73	6,46	0,14	51,41
8	24,81	15,88	6,47	0,09	48,18
9	26,02	15,43	6,58	–	48,02
Refiltered oil					
10	23,12	15,09	6,49	0,07	44,77
11	22,97	15,85	6,54	0,09	45,45
12	22,53	13,33	5,44	–	41,30
13	23,34	12,63	5,18	–	41,20
Polymers					
14	235,90	28,88	19,42	0,73	84,93
15	34,41	34,62	17,08	0,75	86,87
16	35,55	28,01	10,47	0,43	74,47
17	36,27	28,60	11,51	0,46	76,84
18	35,92	27,40	10,49	0,10	73,91

Σ HBC – sum of components which boiling temperature is higher than 270 °C

The data presented in the table allow us to determine a raw materials base for obtaining acenaphthene, diphenylene dioxide, fluorene. Low content of fractions 270...300 °C (table 1) does not permit to consider straw oil as material for emission of listed components without pretreatment.

Such pretreatment is carried out in regenerator. In this case, high-boiling components content increases in 1.5...2 times in comparison with fresh and reverse oil.

Sum total of the components boiling away at more than 270 °C reaches 80 wt. % and more in polymers. Maximal quantity of target component (fluorene) is observed in the products segregated at the beginning of regeneration cycle (pos. 14, 15). At the end of the cycle decrease of total yield of high-boiling components is observed mainly due to fluorene yield reduction.

Polymer selection at the initial cycle of regeneration is optimal from the position of recycling for fluorene extraction (pos. 14, 15). In case of polymer recycling into another individual components selection time is not of considerable importance.

Generalizing the materials obtained by researching of straw oil and polymers composition regeneration process laboratory investigations in developing of technology of fluorene extraction from polymer should be divided into two stages.

The first is the 270...310 °C long distillate extraction for forerunning and properly polymers removal.

The second one is a long distillate rectification at control of products composition at different temperatures.

The 270...310 °C long distillate extraction was carried out in Wurtz bulb. Distillation material balance is presented in table 3.

Table 3. *Polymers breakup*

Fraction	Wt. %
Recovery to 270 °C	18
Long distillate 270...310 °C	60
Vat residue >310 °C	22

A long distillate was cooled and centrifuged for crystal phase and oil extraction. Crystals and oil were undergone the chromatographic analysis.

The results of the analysis showed that naphthalene, dimethylnaphthalenes, diphenyl, acenaphthene, dioxide diphenylene and fluorene entered into the composition of oil and crystals. Increased content of high-boiling component in crystals differs them from oil that indicates that fluorene concentration in solid phase occurs already on the stage of crystallization.

Crystal part of 270...310 °C fraction separated after oil extraction was subjected to rectification. Rectification was carried out at the laboratory packed

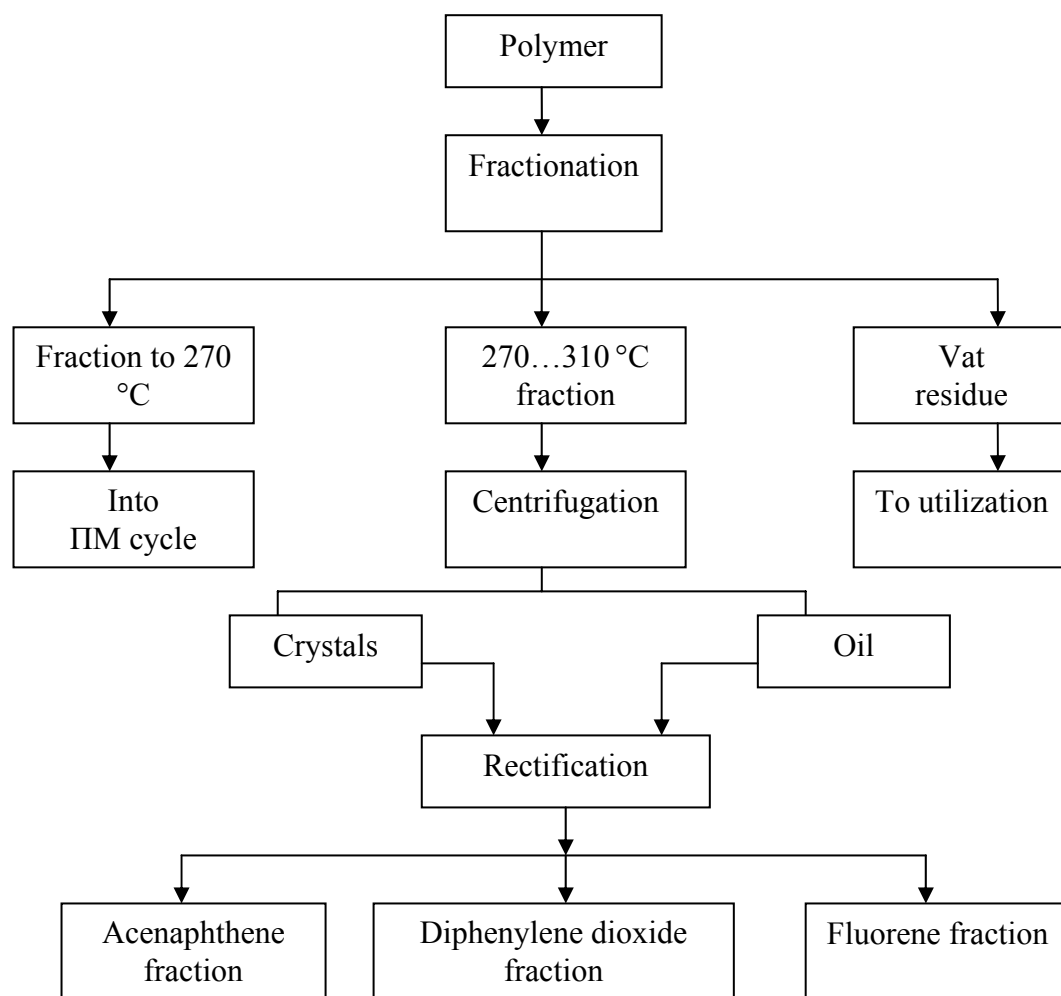


Figure. *Flow scheme of polymers technological recycling*

rectifying column with Levin head. Column effectiveness is 50 theoretical plates. Owing to close boiling temperatures of main components high reflux ratio is recommended at extraction. It was achieved by selecting ball refluxes of different diameters (from 40 to 60 mm) with natural air cooling. Vapor phase temperature was measured in immediate vicinity of the place of product selection.

Composition of products distilled at rectification was controlled by sampling in the range of 270...300 °C with a 5° step and analysis at chromatograph JIXM-8MД. The results of the analysis are presented in table 4.

Table 4. Individual components content at rectification of long distillate crystal part

Component	Component content, wt. %, at selection temperature, °C									
	260	265	270	275	280	285	290	295	297	300
Diphenyl+dimethylnaphthalene	86,7	83,4	39,1	11,0	1,5					
Acenaphthene	12,4	16,6	60,9	89,0	72,0					
Diphenylene dioxide					26,5					1,5
Fluorene						85,2	56,0	18,9	7,8	94,3
Anthracene						14,8	44,0	81,1	92,2	4,2

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The obtained data allow us to restrict roughly temperature intervals of individual components extractions at batch rectification by the following limits:

acenaphthene – 270...280 °C;
diphenylene dioxide – 280...290 °C;
fluorene – 290...300 °C.

Thus, flow scheme of polymers technological recycling may be presented in the following way (figure).

Conclusion

- In the given conditions yield and composition of straw oil fractions from different parts of flowsheet are examined.
- It was mentioned that polymers of benzene extraction from regeneration cycle of straw oil are the most acceptable as raw material for acenaphthene, diphenylene dioxide and fluorine extraction.
- Laboratory researches of long fraction 270...300 °C composition at its rectification were carried out.
- Flow scheme of technological recycling of by-product – coking industry wastes obtaining individual compounds – acenaphthene, diphenylene dioxide and fluorine was suggested.