

NITROGEN BASES IN THE COKING PRODUCTS OF COAL
(COMPOSITION, METHODS OF ISOLATION,
AND UTILIZATION)
(REVIEW)

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The compositions and yields of nitrogen bases during thermochemical transformations of the organic mass of coals are presented. The dependence of the distribution of nitrogen in the products of thermal refining of coal on the type of field, the degree of metamorphism, and the coking temperature is demonstrated. The percentages of nitrogen bases in the coking products, the composition of the base fractions, and a list of reagents of the pyridine and quinoline series developed in the USSR are presented. The industrial methods for the isolation of the nitrogen bases from coking gas and coal tar in the USSR and abroad and numerous studies on the development of methods for the isolation of the bases and their analysis are described. Possible ways to use the bases and resources for increasing their production are indicated.

Nitrogen bases, which are isolated with coking gas and coal tar, are formed during thermochemical transformations of the organic mass of coals during coking. The compositions and yields of the gaseous products depend both on the composition of the coal and on the coking conditions. The percentage of nitrogen in coal varies from 0.2 to 3.0% [1]. Coals with a high degree of metamorphism, for example, anthracites, contain less nitrogen (0.2-1.5%) than the youngest coals, for example, lignites (0.4-2.5%).

The percentage of nitrogen in coals from various fields of the USSR ranges from 1 to 3%, and the maximum percentage of nitrogen is characteristic of coals from the Kuznetsk field, whereas the minimum percentage of nitrogen is characteristic of the coals of the Kizel field [2-5]. It is supposed that the nitrogen in the coals enters primarily into the composition of heterocycles, whereas NH_2 and NH groupings, which do not enter into the composition of the heterocycles, are present in smaller amounts.

The ratio between the forms of bonding of nitrogen in coal depends on the degree of metamorphism and the conditions under which the coal is formed: Nitrogen of aromatic heterocycles predominates in older coals [6]. The distribution of nitrogen among the products of thermal refining of the coal depends on the type of field, the degree of metamorphism of the coal, and the coking temperature. The nitrogen compounds of Donetsk coals are thermally more stable than Kuznetsk coals, and more nitrogen remains in the coal when they are subjected to the coking process [7] (Table 1).

The effect of the coking temperature on the percentage of bases in the tar can be illustrated by the data in Table 2. The maximum percentage of bases in the tar is encountered at 550-650°C [1], as compared with 800-900° for the more metamorphised coals [8]. The percentage of bases in the tar decreases somewhat as the coking temperature is raised further, and the yield of ammonia increases.

The bases obtained by thermal refining of coal have primarily aromatic character and consist of pyridine and quinoline derivatives; aromatic amines are present in small amounts. The composition of the bases does not change substantially as the coking temperature is raised. There are somewhat more secondary amines and alkyl-substituted pyridines and quinolines in the products obtained at lower coking temperatures. The amount

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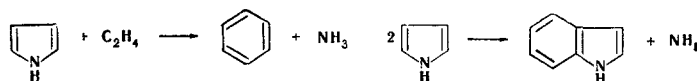
TABLE 1. Distribution of Nitrogen in the Coking

Coals	Coke	NH ₃	HCN	Tar	Gas
Donetsk	58,0	11,0	1,0	2,0	28,0
Kuznetsk	45,0	12,0	0,5	3,5	39,0

TABLE 2. Dependence of the Percentage of Bases in the Tar on the Temperature

Temperature, °C	Percentage of bases in the tar	
	according to data in [1]	according to data in [8]
400	1,62	—
450	2,06	—
500	2,35	1,4
550	2,66	—
600	3,00	1,3
650	3,15	—
700	2,54	1,6
800	—	1,7
900	—	1,8
1000	—	1,5
1100	—	1,1

of alkyl derivatives decreases, the secondary amines decompose, and the amount of ammonia increases at high temperatures. It is assumed [8] that a reaction of the following type occurs in this case:



Isolation and Analysis of the Bases

During cooling of the gaseous coking products, a portion of the bases, the so-called "heavy" bases (primarily two- and three-ring compounds) condenses and enters into the composition of the coal tar. Pyridine derivatives (the "light bases") remain primarily in the gas. They are extracted from the coking gas, together with ammonia, with sulfuric acid and are isolated by distillation from a solution neutralized with ammonia vapors. Depending on the percentage of nitrogen in the coals, the amount of pyridine bases in the coking gas ranges from 0.3 to 1.3 g/m³, whereas the percentage of quinoline bases in the tar ranges from 1 to 3% [9]. In some countries (for example, in England and the Czechoslovakian SSR) the pyridine bases are not extracted from the coking gas along with the ammonia during the production of ammonium sulfate but are transferred to benzene and to the coal tar and extracted from them.

The bases that have been incorporated in the tar are distributed among various fractions during its distillation. Of greatest interest are the quinoline bases that are concentrated in the naphthalene and absorption fractions, from which they are isolated by treatment with 20-25% sulfuric acid and subsequent neutralization of the solution of sulfates with a sodium hydroxide solution, ammonia vapors, or ammonium hydroxide.

A method for the extraction of the bases from the tar fractions by treatment of the latter with monopyridine sulfate has been described. The quinoline bases are isolated from the resulting extract by means of pyridine. The dipyridinium sulfate is fractionated for regeneration of the pyridine and the monopyridine sulfate, which are recycled [10]. It has been proposed that the extraction of quinoline bases from the tar fractions be accomplished with monoammonium phosphate [11] and also that they be isolated by means of cation-exchange filters [12].

The technological schemes and apparatus design for the extraction of the bases and the effect of various factors on the extraction of the bases, particularly the effect of phenols, have been elucidated in detail in a number of handbooks, monographs, and papers [11, 13-16].

The phenols contained in the fractions are capable of reacting with the bases to form adducts, which, although they are decomposed by means of NaOH and H₂SO₄, nevertheless hinder removal of the bases [13, 14]. Considering this, many authors recommend the establishment of a sequence of operations for the isolation of pyridine and phenols as a function of the percentages of phenols and bases [14, 15]. Thus, if the percentage of bases exceeds the percentage of phenols, it is recommended that the bases be extracted first.

TABLE 3. Light Pyridine Bases in the Coking Products

Compound	Percentage, %	Compound	Percentage, %
Pyridine	38.60	1,3,6-Trimethylpyridine	0.49
2-Methylpyridine	12.60	2,3,5-Trimethylpyridine	0.14
3-Methylpyridine		3-Vinylpyridine	0.17
4-Methylpyridine	10.80	2-Methyl-5-vinylpyridine	0.29
2-Ethylpyridine	0.05	Aniline	8.59
2,6-Dimethylpyridine	2.84	2-Methylaniline	1.02
2,5-Dimethylpyridine	1.33	4-Methylaniline	0.92
2,4-Dimethylpyridine	4.44	3-Methylaniline	1.99
2,3-Dimethylpyridine	0.57	Quinoline	11.60
3,5-Dimethylpyridine	0.15	Isoquinoline	1.88
3,4-Dimethylpyridine	0.36	2-Methylquinoline	0.24
2,4,6-Trimethylpyridine	0.88		

TABLE 4. Percentage of the Bases in the Gases from Various Plants (g/m³) [22]

Bases	Karaganda	Magnitogorsk	Nizhnetagil'-skii	Chelyabinsk
Pyridine	0,151	0,176	0,246	0,182
2-Picoline	0,032	0,042	0,054	0,042
2,6-Lutidine	0,002	0,012	0,015	0,007
3-Picoline	0,011	0,013	0,013	0,008
4-Picoline	0,013	0,012	0,019	0,010

Approximately 100 nitrogen-containing compounds of aromatic and heterocyclic character have been detected in the chemical products of coking [17].

Gas-liquid chromatography (GLC) methods have become widely used for the determination of the composition of the pyridine bases [18-22]. Nearly the complete composition of the light pyridine bases of one of the eastern plants of the USSR has been determined by Yu. N. Popov [23] (Table 3).

The ratio of the components of the light pyridine bases in the gas depends markedly both on the type of coal and the coking conditions and on the isolation conditions (Table 4), but pyridine remains the main product in all cases, and methylpyridines, 2,4- and 2,6-dimethylpyridines, and aniline predominate in the remaining products (Tables 3 and 4) [24].

The composition of the bases of coal tar has been determined by many researchers [25-31]. Especially reliable results have been obtained by GLC [32-40]. The presence of ~120 compounds in amounts ranging from 0.03 to 61.5% was established in the most detailed study made by Yu. N. Popov [32]. The structures were ascertained for 68 basic compounds constituting 96% of the total amount of material, and group affiliations were determined for the remaining compounds. The percentages of the main components in the bases isolated from the naphthalene and absorption fractions are presented in Table 5.

The percentage of components in the bases of the naphthalene and absorption fractions may vary considerably as a function not only of the equality of the tar but also of the conditions used in its distillation and in the isolation of the bases [38]. However, under all circumstances, the main components remain quinoline, isoquinoline, 2- and 4-methylquinolines, and indole.

A considerable number of bases are contained in the anthracene fraction (up to 7%). They consist of high-boiling homologs of quinoline and isoquinoline, acridine and its derivatives, and naphthylamines. The major component of these bases is acridine. Its percentage in the bases isolated from the tar fractions selected during its distillation to 350° ranges from 7 to 8%, whereas the percentage of quinoline amounts to only 10%. Thus acridine is the second most prevalent base of coal tar [41].

Refining of the Pyridine Bases

The greatest attention in refining is directed to the isolation of the components present in considerable amounts: pyridine and its monosubstituted derivatives and some dimethyl-substituted derivatives.

TABLE 5. Percentages of the Main Components in the Bases of the Individual Fractions of the Tar and in the Tar

Components	Percentage			
	in bases of naphthalene fraction [32]	in bases of absorption fraction [32]	in bases of anthracene fraction [41]	in the tar [40]
Quinoline	61,50	28,40	—	0,32
Isoquinoline	13,02	13,50	—	0,1—0,2
2-Methylquinoline	7,31	9,54	—	0,1
4-Methylquinoline	0,27	3,43	—	0,016
Indole	0,41	12,50	—	0,2—0,4
8-Methylquinoline	—	1,33	—	0,004
6-Methylquinoline	1,26	8,03	—	—
7-Methylquinoline			—	—
3-Methylquinoline	0,56	1,11	—	—
Acridine			14—16	0,20—0,25 ⁴¹

TABLE 6. Composition of the Fractions of the Bases of the Pyridine Series Generated on an Industrial Scale in the USSR

Substance	bp range, °C	Percentage					
		pyridine	α -picoline	β -picoline	γ -picoline	2,6-lutidine	other lutidines
Pure pyridine (GOST 27-47 2-67)	114—116	98,0	—	—	—	—	—
Pyridine-solvent (ChMTU 6-49-70)	120—140	12,5	74,0	2,0	2,0	2,1	4,5
β -Picoline fraction (TU 14-6-88-73)	138—146	—	10,2	32,4	36,3	21,0	—

Pyridine, pyridine-solvent, and the β -picoline fraction, which are commercial products and also serve as the starting materials for the isolation of the individual substances, are obtained as a result of primary rectification of the anhydrous light pyridine bases. The approximate composition of the fractions and a list of the technical standards for them are presented in Table 6. Where the production of higher-boiling compounds is necessary, the lutidine (bp 158–167°) and collidine (bp 168–171°) fractions are selected during rectification.

Many studies have been made on the development of methods for the isolation of β - and γ -picolines, since they are required in large quantities. There have been reports that the individual substances with a degree of purity of 99% in yields of 70–87% can be obtained from the resources by azeotropic rectification with water [42, 43]. This method does not require the use of other reagents but a highly effective rectification column and high heat consumption are necessary. A similar process has been realized in England under industrial conditions with a column with an efficiency of 100 theoretical plates, but only 2,6-lutidine was isolated in this case, and the β - and γ -picolines were not separated [44].

It has also been proposed that rectification be carried out in the presence of ammonium salts [45] and an aqueous solution of sulfur dioxide [46], with lower aliphatic acids [47], and with phenols [48]. There is also a method for the separation of the β -picoline fraction by extractive rectification with glycerol [49]. Methods for the separation of the β -picoline fraction by extraction with two solvents [11, 50, 51] and by contact with molecular sieves [52] have been described. These methods have not found practical application.

One of the methods for the processing of the β -picoline fraction, which has been accomplished under industrial conditions, consists of its rectification with an aqueous solution of formaldehyde. In this case the azeotropes of the individual components are distilled in the following order: pyridine, α -picoline, 2,6-lutidine, and β -picoline. γ -Picoline undergoes condensation with formaldehyde and remains in the rectification still. Isonicotinic acid is obtained by oxidation of the hydroxymethylol derivative of γ -picoline with nitric acid, and β -picoline, after its isolation through a complex salt with copper sulfate, is oxidized by permanganate to nicotinic acid [53]. This method is used in plants that produce medicinal preparations. It was convenient until isonicotinic acid became necessary for the production of phthivazide. At present, the need for this preparation has decreased sharply, and the use of γ -picoline is fraught with difficulties. In this connection, a further search for economical methods for the isolation of the components of the β -picoline fraction in pure form is necessary.

The numerous methods for the isolation of the homologs of pyridine based on complexing [54–64] are not suitable for large-scale production because of the high outlay of reagents, the multistep character of the processes, and the considerable amount of waste products; however, these methods have found application for the large-scale production of reagents.

Thus, despite the fact that many methods have been proposed for the isolation of the major components of pyridine bases, only pyridine and α -picoline are obtained in pure form in the USSR, and the production of the other substances on a large scale gives rise to difficulties because of the complexity and noneconomical character of the methods; this is due to the similar physical and chemical properties of the components of the bases. A considerable portion of the bases are therefore produced in the form of technical mixtures. In other countries (England [44, 65], Czechoslovakia [66], Poland [67, 68], and the Federal Republic of Germany [69]), the individual substances, except for pyridine, are obtained from the pyridine bases only as reagents in small amounts.

The separation of the β -picoline fraction for the preparation of reagents consists of the successive isolation of, initially, 2,6-lutidine in the form of a complex with urea, after which, after separation of this complex, the β -picoline is precipitated from the filtrate as a complex with cuprous or cupric chloride, the complex is removed by filtration, and the γ -picoline is isolated from the filtrate as a complex with calcium chloride [54]. A method for azeotropic rectification with water has been developed for the isolation of the 2,4-lutidine from the lutidine fraction [70]. The isolation of 2,4-lutidine as the hydrochloride [54] or as a complex with cupric chloride [71] is possible. 2,3-Lutidine is precipitated by phosphoric acid from a solution of the lutidine fraction in ethanol [55, 72]. Its isolation is also possible as a complex with urea [73]. 2,5-Lutidine was isolated through a complex with phenol [11], whereas 3,5-lutidine was isolated through the quaternary salt with 2,4-dinitrochlorobenzene [11]. 2,4,6-Collidine can be extracted from the collidine fraction as the hydrochloride after preliminary removal of aniline [54], as a complex with a copper salt [71, 74], or through the phosphate [72, 75].

A method for sorption purification on AN-18 anion-exchange resin with subsequent rectification has been developed for the preparation of reagent-grade pyridine [76]. α -Picoline of reagent purity is obtained by single rectification of the pyridine-solvent, with selection of the fraction with bp 128-130°. It has been proposed that finer purification of α -picoline be achieved by precipitation as complexes with zinc chloride [77], copper perchlorate [78], and selenium dioxide [79].

A list of the reagents produced from natural bases in the USSR, methods for their preparations, and the technical standards for them in force in 1975 are presented in Table 7.

Refining of the Quinoline Bases

The resources of quinoline bases are considerably greater than those of the pyridine bases. The main component in them is quinoline. In the Federal Republic of Germany (FRG), for example, 6000 tons of quinoline can be obtained from the coking products [80], as compared with 10,000-12,000 tons in the USSR [81], but the processing volume of the bases is low.

A mixture of bases isolated from the naphthalene and absorption fractions is rectified in a periodic process with a column having 50 plates at 500-600 mm, and technical-grade (90-93%) quinoline is obtained in 70-74% yield from the resources [82]. The principal impurity in the technical-grade quinoline is isoquinoline (5-6%), and it also contains ~1% primary amines and 1-2% neutral oils. The boiling point of the technical-grade quinoline ranges from 235.5 to 238.5°. The isolation of quinoline can also be accomplished by a continuous scheme if the amount of bases being processed is such that the continuous process is economically advantageous [83].

In addition to quinoline, an isoquinoline-quinaldine fraction, containing ~40% isoquinoline and as much quinaldine, and a lepidine fraction, containing ~20% lepidine and 15-17% indole, can be obtained by rectification. The fractions are used for the isolation of the individual substances of reagent purity. A portion of the technical-grade quinoline is also used for the preparation of reagent-grade quinoline [84].

The names of the reagents obtained in the USSR from the bases from coal tar, the technical standards for them in force, and the methods for their preparation are presented in Table 8. In addition to the data enumerated in Table 8, a number of methods for the isolation and purification of quinoline are also described.

Quinoline with a purity of 98% was obtained in 87.5% yields from technical-grade quinoline, freed of non-basic impurities, by low-vacuum rectification with a column with an efficiency of 20 theoretical plates [85]. Quinoline with a purity of 95-97% was obtained in 77-90% yield by rectification of the bases with a column with an efficiency of 40 theoretical plates [37]. Pure quinoline can also be obtained from the quinoline fraction by azeotropic rectification with ethylene glycol [86] or the kerosene fraction of petroleum [87].

Studies in which the different solubilities of the quinoline and isoquinoline salts with mineral or organic acids in water or ethanol [88-93], differences in the basicities of quinoline and isoquinoline [94], and differences in the temperatures of crystallization of their hydrates [17, 95] are used for the isolation of pure quinoline are known.

TABLE 7. List of the Reagents from the Light Pyridine Bases Manufactured by the Nizhnetagil'skii Metallurgical Combine, Technical Standards for Them, and Methods of Isolation

Reagent	Technical standards	Method of isolation
Pyridine	GOST 13647-68	Filtration through an ion-exchange filter and distillation
α -Picoline	TU 6-09-3037-73	Rectification
β -Picoline	MRTU 6-09-4882-67	Precipitation of the complex with cupric chloride
γ -Picoline	MRTU 6-09-4582-67	Precipitation of the complex with calcium chloride
2,6-Lutidine	TU 6-09-3640-74	Precipitation of the adduct with urea
2,6-Lutidine	MRTU 6-09-6357-69	Precipitation of the hydrochloride
2,4,6-Collidine	MRTU 6-06-6356-69	Precipitation of the hydrochloride
2,3-Lutidine	MRTU 6-09-6082-69	Precipitation of the phosphate

TABLE 8. List of Reagents from the Heavy Pyridine Bases Manufactured in the USSR, Technical Standards for Them, and Methods of Isolation [84]

Reagent	Technical standard No.	Method of isolation
Quinoline	MRTU 6-09-6233-69	Precipitation of the phosphate from water
Isoquinoline	MRTU 6-09-4671-67	Precipitation of the sulfate from a solution of the bases in ethanol
Quinaldine	MRTU 6-09-6234-69	Precipitation of the adduct with urea
Lepidine	MRTU 6-09-4672-67	Precipitation of the sulfate from a solution of the bases in ethanol
Technical-grade indole	TU 14-6-54-71	a) Extraction with benzene from an aqueous solution of the sulfate of the bases b) Fusion with KOH
Pure-grade indole	TU 6-09-2442-72	Recrystallization of technical-grade indole

From the isoquinoline fractions one can obtain 93-96% isoquinoline by rectification with a column with an efficiency of 80 theoretical plates [37]. The differences in the basicities of isoquinoline and quinoline [96-98] and in the solubilities of their salt with mineral acids [99, 100] can also be used for the isolation of isoquinoline. It has been proposed that isoquinoline be isolated as complexes with metal salts (cupric chloride, cobaltous chloride, zinc chloride, calcium chloride, etc.) [101-105].

A method based on the ability of quinaldine to form a stable adduct with urea has been found to be the most effective method for the isolation of quinaldine [106-108]. In addition, methods for the isolation of quinaldine as the hydrochloride [109], through a complex with phenol or its homologs [11], and by fractional crystallization of the hydrates [17] have been described.

In the preparation of reagent-grade lepidine, it is isolated as the sulfate, which is then decomposed [110]. There is a communication that lepidine can be isolated in the form of an adduct with *o*-cresol [111] or with urea [112].

It has been proposed that the isolation of 5-methylquinoline be carried out in the form of its complex with cupric chloride [113] and that 2,4-dimethylquinoline be isolated in the form of its sulfate [11] from the appropriate narrow fractions.

A method based on the difference in the basicities of indole and the accompanying bases can be used for the isolation of indole from a mixture of bases. The method consists of dissolving the appropriate fraction of the bases in benzene and tying up the bases with 10-15% sulfuric or hydrochloric acid. The less basic indole remains in the benzene solution and is isolated from it after removal of the benzene by distillation [114-116]. Indole can also be isolated directly from the absorption fraction of coal tar [117] or from the narrow fraction obtained by distillation of the absorption fraction and by fusion with potassium hydroxide [118, 119]. The alkaline fused mass, after separation from the unchanged portion of the crude material, is hydrolyzed with water, and the liberated indole oil is rectified in the first case and distilled in the second. The distillate is crystallized and centrifuged; however, where necessary, it is recrystallized from ethanol.

Indole can also be isolated by treatment of the appropriate fraction with 35% sulfuric acid [120-121] and also by means of preparative chromatography [122, 123]. The latter method is extremely tempting, since it does not require the consumption of expensive and difficult-to-obtain reagents and does not give harmful waste

products. The impurities that accompany indole (methylnaphthalenes, diphenyl, and other components of coal tar) are separated in the form of enriched fractions, which can be used either for the isolation of the individual compounds or converted to coal tar oils. In industry, technical-grade indole is isolated primarily by alkaline fusion from the narrow fraction isolated during rectification of the absorption fraction of the tar [119] and in small amounts from the quinoline bases by the method described in [114, 115].

Acridine can be isolated from the thoroughly filtered anthracene oil with 24% bisulfite solution. The bisulfite solution is purified by passing it through a coke filter, and the compound thus formed is decomposed with alkali [124]. Acridine can be obtained from a mixture of the bases of the anthracene fraction by rectification and crystallization from benzene [125]. Acridine is currently not isolated on an industrial scale in the USSR. In the Czechoslovakian SSR and the Federal Republic of Germany it is obtained in small amounts as a reagent [68].

Utilization of the Bases

The pyridine and quinoline bases are used in the form of the individual components or technical-grade mixtures. Pyridine is used as a solvent, in the manufacture of waterproof fabrics, and for the synthesis of herbicides, fungicides, bactericides, and medicinal preparations. Dipyridyl herbicides, for example, diquat and paraquat [126, 127], on the basis of pyridine are manufactured on an industrial scale. Quaternary pyridine salts are used as wetting agents, dispersing agents, emulsifying agents, and as an antistatic agent in the spinning of artificial silk [128].

A considerable amount of pyridine is hydrogenated for the manufacture of piperidine, which on reaction with carbon disulfide gives a dithiocarbamate. Its sodium or divalent metal salts are strong accelerators for the vulcanization of rubber [44].

Surfactants of the pyridine series have assumed great significance. In the USSR, technology for the preparation of an effective surfactant - katapin (alkylbenzylpyridinium chloride), which is a highly effective bactericide (its effectiveness is higher by a factor of 10 than that of calcium hypochlorite and phenol) - has been developed in the USSR on the basis of pyridine. Katapin also has strong inhibiting properties, and it is an extremely effective inhibitor in the poisoning of ferrous metals. The use of katapin in polychlorovinyl compositions for the preparation of coating plates and linoleum and as surfactants in the manufacture of rubber articles is possible [129].

A portion of the pyridine manufactured by the by-product coke industry of the USSR is exported to a number of countries [130].

The β -picoline fraction is used completely in the pharmaceutical and vitamin industry [131]. The most nearly complete utilization of γ -picoline is achieved by treatment of the fraction with formaldehyde and subsequent separation of the mixture of methylol derivatives and oxidation of them with nitric acid. The resulting isonicotinic acid is the principal intermediate in the manufacture of antituberculous preparations of the isonicotinic acid hydrazide series (isoniazid, metazid, phthivazide, saluzid, etc.), monoaminoxidase inhibitors (iprazid and niamid), and original medicinal preparations of the quinuclidine series - atseklidin (kholinomimetin, used in ophthalmology, surgery, and obstetric-gynecological practice), oksilidin (sedative and hypotensive agent used in the therapy of hypertonic disease and in the case of psychic disturbances), and kvallidil (a curarelike preparation of competitive activity used in surgical practice). β -Picoline is the raw material for the manufacture of well-known vitamins - nicotinic acid and its amide - and for the preparation of kordiamin and nikodin. Methods have been developed for the preparation of original ganglion-blocking agents - dimekolin and nanofin - from 2,6-lutidine.

One of the most important derivatives of the pyridinecarboxylic acid series is tordon or picloram (3,5,6-trichloro-4-aminopicolinic acid). Tordon (the Soviet analog is khloramp) is obtained from α -picoline by chlorination, treatment with ammonia, and saponification [127].

Vinylpyridines are assuming ever increasing importance in the chemical industry owing to their high reactivities and ready polymerizability. The methods for the preparation of vinylpyridines in most cases are based on the use of alkylpyridines as starting materials. The basis for the preparation of vinyl-substituted bases is the condensation of the corresponding picolines, lutidines, collidines, and methylquinolines, which have an active methyl group in the 2, 4, or 6 positions, with formaldehyde and subsequent dehydration of the resulting carbinols [132, 133]. The residues from the isolation of the technical-grade and pure-grade products of the pyridine series are used as a component of the VNINP-106 additive to sulfurous petroleum residues, leading to combustion, and for the prevention of corrosion of the external surfaces of the tubes of steam boilers [9]. Of the coal tar bases, quinoline is acquiring great significance as a cheap and easy-to-obtain raw material for the prepara-

tion of nicotinic acid. In the manufacture of nicotinic acid, quinoline competes with β -picoline and 2-methyl-5-ethylpyridine as a raw material [80]. The United States produces 35,000 tons of nicotinic acid per year; it is obtained in part by oxidation of quinoline with nitric acid [134]. Studies intended to improve this process are continuing [135]. Polish researchers have made exploratory and semi-industrial studies on the preparation of nicotinic acid [136]. Studies involving the oxidation of quinoline with ozone in a nitric acid medium are known [137]. All of the known methods for the preparation of nicotinic acid from quinoline have a substantial drawback — the use of nitric acid as the oxidizing agent, which creates difficulties in connection with the high corrosiveness of the medium, the large amount of waste products, and the complexity involved in the isolation of the desired product. A method for the preparation of nicotinic acid by ozonolysis of quinoline is therefore of promise [81].

Another use of quinoline is the synthesis of 8-hydroxyquinoline (oxine). Its manufacture from quinoline was organized in the Federal Republic of Germany [80]. The technology for its preparation from coal tar quinoline was developed in the USSR [138]. Salts of 8-hydroxyquinoline with metals and acids, often in the form of copper 8-hydroxyquinolate (copper oxinate) and 8-hydroxyquinoline sulfate (khinozol) or 8-hydroxyquinoline benzoate, are used for the protection of plants. Khinozol [139], yatren (a mixture of 7-iodo-8-hydroxyquinoline-5-sulfonic acid with sodium bicarbonate) [140], eneroseptol (5-chloro-7-iodo-8-hydroxyquinoline), etc., are used in medicine as antiseptics and in the treatment of amebic dysentery and other diseases. 8-Hydroxyquinoline and its derivatives are used in analytical chemistry [141, 142] for the isolation and purification of uranium [143]. It has been proposed that copper oxinate be used as a wood pulp antiseptic [144].

Many derivatives of the products of hydrogenation of quinoline can be used as repellents [145-148]. Quaternary quinoline salts are fundamentally cationic surfactants and enter into the composition of detergents, disinfectants, and stabilizing agents, as well as emulsifying, dispersing, and wetting agents [149, 150].

The residue of the bases remaining after isolation of quinoline finds practically unlimited application as a component of the VNIINP-106 additive to sulfurous petroleum residues that lead to combustion, and is used in small amounts as an inhibitor of acid corrosion in the poisoning of ferrous metals. Isoquinoline has not yet found application and is used only as a reagent, although many of its derivatives are physiologically active substances.

A method is being developed for the preparation of ion-exchange resins based on the isoquinoline contained in the isoquinoline-quinaldine fraction. This method is based on the different reactivities of quinoline and isoquinoline in reactions with alkyl halides. In this case, one observes selective extraction of isoquinoline from the technical fraction in the form of a polymeric quaternary salt — a highly basic anion-exchange resin [151].

Quinaldine is of interest for the preparation of cyanine and isocyanine dyes. Quinaldinic acid, obtained from quinaldine, finds application as a reagent in analytical chemistry. Interesting physiological properties of sulfur derivatives of quinaldinic acid are noted in [152]. 2-Vinylquinoline [153, 154], which can be used for the preparation of oil-resistant rubbers, ion-exchange resins, and other polymeric products, is synthesized by the reaction of quinaldine with paraformaldehyde and subsequent dehydration of the resulting carbinols. There are data [155] that quinaldine has high activity as a leveling additive in nickel plating.

The preparation from lepidine of dyes that are excellent photosensitizers is possible [156-159]. Quinoline-4-carboxylic (cinchoninic) acid is synthesized by oxidation of lepidine [166], and a number of its derivatives are used as therapeutic preparations.

Indole is currently generating a great deal of interest owing to its derivatives, which are the basis of many pharmaceutical preparations, dyes, bactericides, pesticides, and other products of organic synthesis [160-164], as well as tryptophan. Indole can serve as a raw material for the synthesis of plant-growth stimulators [β -indolylacetic acid (heteroauxin) and 3-indolyl- γ -butyric acid [127]].

In analyzing the state of the manufacture and the need for pyridine bases from coking products, one may note that there are contradictions between the resources and the need. The need for some pyridine bases considerably exceeds their resources in the coking products, despite the fact that the manufacture of pyridine in the USSR has increased in the last 15 years by a factor of 18, whereas the manufacture of the β -picoline fraction has increased by a factor of five. A certain reserve in the increase in the production of pyridine bases in the USSR exists due to an increase in their extraction from gas, since the degree of extraction currently does not exceed 70%. Nevertheless, as McNeil noted in 1965 [65], the need for pyridine bases has increased to such an extent that only direct synthesis will satisfy it. In this connection, synthetic methods for the preparation of pyridine and its homologs are being developed and realized in many countries — Japan, England, Italy, the Federal Republic of Germany, etc. Thus, 65,000 tons of pure pyridine and α -, β -, γ -picolines have been obtained

in Japan [165]. The organization of the manufacture of synthetic pyridine bases is also planned in our country. In this connection, the search for methods for the preparation of pure products of the pyridine series from coal tar raw material is not being developed, but a considerable amount of them will be used as technical mixtures.

The situation with regard to quinoline bases is different — only a very small portion of the resources of these substances in the coking products is being isolated and refined. Detailed information regarding the refining of quinoline bases is available in a review [40]. Vymetal feels that synthetic methods for the preparation of quinoline and its derivatives are more complex and more costly than their isolation from coal tar. It therefore seems expedient to expand the use of quinoline for the preparation of 8-hydroxyquinoline and nicotinic acid; this makes it possible to reduce the deficit of β -picoline in the manufacture of the latter. Moreover, the cost of quinoline is substantially lower than that of synthetic β -picoline.

The following compounds are among the nitrogen-containing compounds that could be obtained from coal tar raw material and used for organic synthesis but are currently not isolated or are isolated in very small amounts and used only as reagents: 2,3-, 2,4-, 2,5-, and 2,6-dimethylpyridines, 2,4,6-trimethylpyridine, isoquinoline, quinaldine, lepidine, indole, and acridine. The isolation of these components of the bases in pure form is not as simple as the isolation of quinoline and pyridine, and their industrial utilization would therefore be possible on the basis of enriched crude fractions, as, for example, selective extraction of isoquinoline from the crude fraction in the form of the polymeric quaternary salt or selective extraction of quinaldine from the crude fraction in the form of the methylol derivative.

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