Chemistry and Technology of Fuels and Oils, Vol. 36, No. 4, 2000

TECHNOLOGY History of Processes

ASPHALT PRODUCTION TECHNOLOGY. RECENT HISTORY AND OLD PROBLEMS

E. V. Ippolitov and I. B. Grudnikov

UDC 665.637.8:62(09)

The study of the history of engineering is not only due to purely cognitive interest in the past but also to the realization of a fact which has finally become inarguable to us: "one who does not know the past will not see the future." This article is dedicated to the development of domestic asphalt production technology in the final third of the century. The subject and time were selected for both subjective and objective reasons. On one hand, we have not only been witnesses to but also participants in the events that took place in this area in the indicated period of time. On the other hand, the properties of the initial feedstock changed significantly during this period (mixed West Siberian crudes became the fundamental feedstock), which exacerbated the existing process problems and stimulated attempts to solve them. Data from monographs and reviews published in the central press and articles from the journals Khimiya i Tekhnologiya Topliv i Masel [Chemistry and Technology of Fuels and Oils] and Neftepererabotka i Neftekhimiya [Petroleum Refining and Petrochemistry] were used, since the most important events and findings must have been included in these publications. Great attention is focused on the developments which significantly affected the subsequent evolution of asphalt production technology.

QUALITY OF COMMERCIAL ASPHALTS

Product quality is one of the most important characteristics of any plant. The quality of asphalts is regulated by the corresponding state standards which are revised periodically. In comparing the requirements for the quality of paving asphalts, the basis of the domestic standards in different years, it is necessary to point out a curious characteristic: the requirements for the softening point of asphalts with the same penetration at 25°C were stiffened for a certain time, then relaxed.

For different grades of asphalts with penetration of 100×0.1 mm, the lower limit of the softening point was (°C): in 1946: 35 and 40 (GOST 1544-46); in 1952: 40 and 45 (GOST 1544-52); in 1966: 45 (GOST 11954-66); in 1972: 45 (GOST 5.1721-72); in 1976: 40 and 43 (GOST 22245-76) [1]. According to the current GOST 22245-90, the values should not be below $41 - 43^{\circ}$ C [2].

Since the country has not moved from one climatic belt to another, the change in the quality requirements for these products could only be due to changes in the asphalt concrete and asphalt production technologies or in the concepts of the leading scientific schools concerning the optimum values of their properties. The point is that asphalt is a substance with a long lifetime, so that the inaccuracy or accuracy of estimating certain quality indexes will only become evident after several years.

In the late 1960s-early 1970s, extensive practical experience in utilizing different paving asphalts was generalized at the All-Union Scientific-Research Institute of Highways. Their technical properties are determined by the colloidal structure. When the structure is altered in some way, some indexes of the technical

Ukhta Refinery; Ufa State Petroleum Engineering University. Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 4, pp. 18 – 24, July – August, 2000.

properties improve, while others become worse. Quality asphalt should be characterized by the optimum ratio of the values of these indexes, that is, the optimum structure.

A. S. Kolbanovskaya revealed two very different types of asphalt structure [3]. The first type is a coagulation network of asphaltenes, found in a dispersion medium weakly cross-linked with resins, consisting of paraffinic-naphthenic and aromatic hydrocarbons. The second type is a stabilized dilute suspension of asphaltenes in a dispersion medium strongly cross-linked with resins.

The structure of asphalt is predetermined by its group chemical composition. Asphalts of the first type contain more than 25 wt. % asphaltenes and less than 24% resins; asphalts of the second type contain up to 18% asphaltenes and more than 36% resins. The asphalts occupying an intermediate position in group chemical composition (average concentration of asphaltenes of 21 - 23% and resins of 30 - 34%), so-called asphalts of the third type, are characterized by a structure containing elements of both of the structures mentioned above.

It was concluded that asphalts of the third type have the properties necessary for use as a binder for road-construction materials. Although they do not have high indexes for the individual rheological properties of asphalts of the first and second types, these asphalts also do not have their manifest disadvantages. This classification allowed systematizing the results of the individual observations and served as the basis for selecting directions for further research.

The values of a number of properties were determined and included in GOST 11954-66 based on the results of these studies for production of asphalts with the optimum structure, i.e., primarily of the third type. Similarly, in GOST 22245-76, although the requirements for the softening point of BND asphalts were decreased slightly, they were considered to be of higher quality than BN asphalts with a lower softening point.

The opinion concerning the necessity of producing asphalts with a comparatively high softening point in our country ruled for a long time. The domestic standards differed from the standards of many other countries in this respect [1]. In the technology area, this predetermined an increase in the proportion of oxidized asphalts in comparison to residual and precipitated asphalts (asphalts from deasphalting), since it is easy to obtain asphalts with a high softening point only when an oxidation process is used.

It was found that the degree of vacuum distillation in preparation of vacuum resid for distillation must be decreased to increase the softening point of asphalts from a given crude oil with a given penetration at 25° C. However, it is impossible to obtain asphalts which satisfy the requirements of the standard from many crude oils with any degree of vacuum distillation.

The experience obtained was generalized by V. V. Fryazinov and R. S. Akhmetova. They proposed [4] classifying crude oils by the asphaltene, resin, and solid wax content. Crude oil is considered suitable for production of asphalts by oxidation of vacuum resids if the ratios of the indicated components are within specified limits. This classification is widely used in solving practical problems. However, as repeatedly noted [5, 6], it does not make it possible to formulate requirements for the quality of the vacuum resid delivered for oxidation and determining the yield of asphalt. And finally, the concentration of asphaltenes and resins are not among the indexes used in the general technological classification of crude oils.

The classification of crude oils developed a little later based on the total sulfur and solid wax contents not only allows determining the suitability (or unsuitability) of a crude oil for production of oxidized asphalts, but also indicating the necessary degree of distillation in production of vacuum resid [7]. This makes it possible to find the yield of vacuum resid with the true boiling point (TBP) curve of the crude oil. It is thus possible to solve a number of problems in designing asphalt plants using handbook data on the crude oil without conducting any experiments.

Crude oils with a comparatively high solid wax content are not suitable for production of quality paving asphalts with the traditional "distillation—oxidation" scheme. Directions for utilizing these crudes for asphalt production were sought because of the existence of resources of these crudes alone in some regions of the USSR and in accordance with the characteristics of the refining schemes in individual refineries.

Three directions should be distinguished. First: the simplest, but frequently unaffordable version — pumping low-wax, resinous crude into high-wax crude [8]; second: destroying some of the paraffinic hydrocarbons during preliminary heat treatment of atmospheric resid [9]; third: accumulation of an additional amount of aromatic hydrocarbons in the feedstock during preliminary oxidation of atmospheric resid or flux oil [1, 10].

The ductility of the asphalt obtained is increased in all three cases, that is, the index which does not satisfy the requirements of the standard when the traditional scheme is used improves. The inverse scheme: oxidation of part of the atmospheric resid — its vacuum distillation with the unoxidized part — has been successfully tested at **Batumi Refinery** [11], but due to the changing political and environmental conditions, it has not been used continuously. A simpler — at first glance — inverse scheme is also possible: oxidation and vacuum distillation of atmospheric resid. However, the ductility of the asphalt increases less [1] and the amount of oxidation distillate increases.

With the methods of estimating the cost of vacuum resid (based on a factor of 0.6 of the cost of the crude oil) and setting the price of the asphalt used in the period of planned economics, the asphalt production for refineries was generally unsuitable [12]. The situation was exacerbated by the necessity of obtaining light vacuum resid for production of BND asphalts, which was in conflict with the problem of deepening extraction of distillates in AVT. The impossibility of obtaining BND asphalts from asphalt caused the latter to be used as a component of boiler-furnace fuel. To ensure the given viscosity, an additional amount of light cuts was involved in its composition. The solution of asphalt production problems was a constituent part of research to improve refinery plans.

According to the requirements of the time concerning industrial processing of BND asphalts, a method was developed [13] to produce them by blending vacuum resid with asphalt from deasphalting vacuum resid with light naphtha (pentane). It was hypothesized that the deasphalted product of this process could be processed with qualifications, but this goal was not attained for a number of reasons. The use of deasphalting with naphtha to obtain asphalt as the basic target product is not economically expedient. On the other hand, the research related to determining acceptable amounts of asphalt from deasphalting of vacuum resid with propane in feedstock, i.e., mixed with the vacuum resid, was practically justified. In particular, it was shown in [14, 15] that more asphalt could be contained in the feedstock when the "peroxidation—dilution" method was used.

To increase the efficiency of the crude oil residue refining scheme, the group of problems concerning production of paving asphalts was expanded. In 1981, a study was published which demonstrated the possibility of industrial production of residual paving asphalt of the BN type from domestic crude oil [16]. It was also noted that the residual asphalt production volume in our country will increase due to an increase in the degree of extraction of vacuum distillates [1].

The renewed attention to residual asphalts was due to two circumstances: primary processing of these asphalts [1, 17] from heavy crudes abroad and the debatable superiority of oxidized asphalts. However, it was noted in [18] that when BN asphalts (i.e., basically unoxidized asphalts) were replaced by BND asphalts (i.e., basically oxidized asphalts), the time between pavement repairs increases from 16 to 20 years.

It is necessary to hypothesize that these data were obtained based on ideal conditions of use, since the necessity of more frequent repairs was evident. (Information subsequently appeared in [19] indicating that the almost universal lifetime of new and repaired pavements does not hold: separated disintegrated patches, significant erosion, and spalling begin in the first year of use.)

The recommendation to process BND asphalts with the state quality symbol (SQS) instead of BND asphalts was even less justified: increasing the time between repairs from 20 to 21 years was proposed. This recommendation could only be formally implemented in an administrative-command economy.

At the beginning of the 1990s, it was found that the comparative estimations of the lifetime of BN and BND asphalts are also contradictory among road specialists [20, 21]. The same lifetime of pavements based on residual BN asphalts and oxidized blended BND asphalts was hypothesized [22].

The conflicting character of these opinions is perhaps totally explainable. Not only and not as much differences in the properties of these two types of asphalts as many other factors active during the long time of use affect the lifetime of pavements: waterlogging of the ground; poor bed preparation; perturbation of the granulometric composition and measurement of the components of the asphalt concrete mixture; perturbation of the temperature regimes in preparation of the mixture and laying, compaction, and use of the pavement.

It is also known [23] that different kinds of damage can be longevity criteria: loss of uniformity — crack formation or coloration, loss of shape — plastic strains, and others. Finally, the requirements of the standard for asphalt concrete mixtures probably could not be considered irreproachable, as a recent revision indicates [24]: GOST 9128-97 "Asphalt concrete mixtures" took effect in 1999, replacing GOST 9128-84.

The debate has recently intensified [25 - 27] due to the appearance of asphalts from the Finnish firm Neste, processed according to its own specifications, and asphalts from Bitran Joint Stock Company in Ukhta, processed from Yarega crude in special technical conditions, on the domestic market in place of BN and BND asphalts processed according to GOST 22245-90.

Production of residual asphalts was proposed again in [28]. In addition, developing asphalts based on asphalt from deasphalting of vacuum resid with a mixture of propane and butane was proposed — with dilution of the asphalt with the extract of phenol treatment of the oil cut [28]. Studies directed toward obtaining asphalts from visbreaking residues are being conducted with consideration of the foreign experience in this area [29, 30].

The corresponding process conditions have been developed for standardized processing of these unoxidized (residual, blended, heat-treated) asphalts. In the present conditions, it is not difficult to develop and coordinate them with respect to the characteristics of production of the real product, for example, at Kirishi Refinery.

Paving asphalts are thus now being developed according to different technologies and different standard quality requirements. However, the opinion concerning the best quality of unoxidized asphalts in comparison to oxidized asphalts and the environmental advantages of unoxidized asphalt production technology is indisputable.

As noted above, the effect of other factors on the lifetime of pavements can be more important than the quality of the asphalt. Atmospheric emissions are determined by energy consumption, i.e., by the amount of fuel burned. The power requirements, for example, of a deasphalting unit are much higher than for vacuum resid oxidation units [31, 32]; the same can be said about vacuum distillation and visbreaking processes.

The principle of processing unoxidized asphalts is most expedient when another basic product with a qualified use is simultaneously produced in the unit: exhaustive-distillation vacuum gasoil goes to catalytic cracking and is not pumped into fuel atmospheric resid; the deasphalted product is processed further and is not delivered for additional treatment or blending; increasing the output of distillates is the goal of visbreaking. Otherwise, it is preferable to use simpler technology — oxidation of vacuum resid. In other words, the efficiency of the entire system for refining heavy feedstock and not of the individual units should be the criterion for selecting the technology.

The references to the better road quality abroad, where residual asphalts are primarily used, are counterbalanced by a closer example of a different character: the good state of the Moscow—Domodedovo Airport road refinished by Wirtgen using oxidized asphalt from Yarega crude. The same asphalt was purchased by Wimpey Asphalt Co. for building an airport in Mongolia. The asphalt has thus been used in places far from its production site.

Different examples can also be cited for individual regions with the same climatic conditions. There is different experience in using residual asphalts in road construction in Bashkir — both positive and negative: on one street in Ufa, the pavement rapidly broke down due to rutting.

The last statement can be attributed to perturbation of the residual asphalt production regime, but disintegration of pavement based on oxidized asphalts could be due to the same cause. At the same time, it is more difficult to maintain the production conditions and defined quality of residual asphalts than for oxidized asphalts due to the very small drift of the distillation process.

It is interesting to compare the approaches to assessing the quality of asphalts in Russia and abroad. Positive factors include the use of foreign methods for assessing asphalt quality in Russia and the correspondence of the quality indexes with the requirements of positive standards [25, 33, 34]. This will allow assessing the quality of imported asphalts more reliably and promote export of domestic asphalts.

With respect to the foreign concepts of the optimum technical properties of asphalts, although draft unified standards have been developed in the European countries, the opinions of scientists still do not agree. This is particularly indicated by the variety of methods for assessing thermal stability [35].

There is thus no generally accepted opinion concerning the optimum level of the technical properties of asphalts and rational technology for their production, although the desirability of using certain kinds of crude oils (Venesuel'sk, Yarega types) is indisputable. Large foreign manufacturers are not restricted by determination of the technical properties of asphalts and asphalt concretes and are performing additional tests of asphalt concretes with real loads on a moving wheel simulating the work of pavement in different weather conditions. The companies guarantee the quality of the asphalt only after tests which leave no room for discussion.

This problem will perhaps become less pressing with expansion of the use of asphalt binders modified by polymers instead of asphalts for major highways. Such binders are essentially a different construction material and will thus not be examined here. No data on grey asphalt binders or asphalts with adhesive additives will be reported for the same reason. These additives are usually not incorporated by the manufacturers but by the users of the asphalts applied to the actual stone material.

Roofing and construction asphalts follow paving asphalts in production volume. Much less attention was focused on increasing their quality in the time period examined. However, when it became necessary to increase the plasticity of roofing asphalts (caused [36] by the difference in the softening and brittle points), several methods were proposed for reaching this goal: oxidation of light vacuum resid; addition of vacuum distillate to heavy vacuum resid; oxidation in a tubular reactor and instead of in a still; peroxidation of vacuum resid with subsequent dilution with unoxidized vacuum resid [36 – 38]. Addition of vacuum distillate to vacuum resid is the most effective method.

EFFICIENCY OF OXIDIZING VESSELS

Oxidation was the fundamental process in production of asphalts in the period examined. Different units were used for oxidation.

Vat. This was usually a so-called vat — a periodically operating cylindrical vessel with a low height: diameter ratio. The height of a typical vat with a volume of approximately 200 m³ is equal to 10 m and the diameter is 5.3 m.

As a function of the defined output, a unit was equipped with up to 11 vats [1, 5]. Each one had the necessary control and measuring equipment and a system that ensured safe operation (steam smothering, explosive plates). Graphs of operation of the vats (pumping in feedstock, oxidation, certification, asphalt discharge) were combined so that periodic operation of each one ensured continuous operation of the entire unit.

The vats were sometimes mounted at different heights so that the oxidized mass would flow from one vat into another by gravity: the battery of vats operated continuously. However, due to the bulkiness of this oxidizing unit, it was almost impossible to increase the asphalt production volume, i.e., to solve the problem facing the industry at that time.

As oxidizing equipment, the vat is characterized by low efficiency, i.e., a low degree of utilization of atmospheric oxygen in oxidation reactions: the oxygen content in oxidation gases is 7 - 9 vol. % in production of paving asphalts and 13 - 17 vol. % in production of construction asphalts.

On one hand, this predetermines the high power consumption for production (consumption of electric power for compression of the air for oxidation, consumption of fuel for burning the oxidation gases), and on the other hand causes coking of the walls of the gas space, and ignition and explosion in the gas phase. Ensuring safety from explosion requires constant delivery of an inert gas (nitrogen or water vapor) to reduce the concentration of oxygen to the standardized value.

Another drawback of the vat is frequent coke clogging of the air disperser caused by the periodic operation. When the air feed to the disperser stops at the end of the oxidation stage, asphalt flows into it and is not completely forced out by the air in the following oxidation stage. The asphalt film formed on the inside of the disperser is coked. Changing the vat from periodic to continuous operation eliminates coking of the disperser [39] but does not radically affect the efficiency of utilization of atmospheric oxygen.

It was possible to increase the asphalt production volume by conducting the process in other oxidizing vessels — tubular reactors and hollow columns; as a result, this index increased by 1.4 times in the first half of the 1970s [40].

The tubular reactor is a coil with vertical tubes contained in a cylindrical jacket. The feedstock mixed with air and recirculated substance (asphalt) heated in the furnace enters the coil where it is oxidized in a turbulent air current. The gas—vapor drop mixture coming out of the reactor is fed to an evaporator where it is separated into gas and liquid phases.

The liquid phase — asphalt — is mostly returned to the reactor (recirculated) and in an equilibrium amount is sent to the finished product container. The gas phase is fed through a separator to the afterburner furnace. The thermal equilibrium of the exothermic oxidation process is maintained by feeding a controlled amount of cold air into the jacket with a fan. The degree of utilization of atmospheric oxygen in a tubular reactor is high: its content in the oxidation gases does not exceed 3 vol. %.

The **hollow column** is a cylindrical vessel with a higher height-to-diameter ratio and a greater height than the vat. Air is fed into the column, like the vat, through a disperser positioned in the lower part of the vessel. The oxidation gases exit at the top of the column and are fed into the afterburner furnace through a separator. In contrast to the vat, the column is always included in the continuous oxidation scheme, the feedstock is usually fed into the upper part of the bubble layer, and the asphalt is pumped out at the bottom. The degree of utilization of atmospheric oxygen in the column is a function of the kind of asphalt manufactured: the oxygen content in the oxidation gases is approximately 3% in production of paving and approximately 9% in production of construction asphalts.

We know of no data on use of tubular reactors abroad as hollow columns have been widely used there. In domestic practice, the efficiency of these vessels has not always been unambiguously evaluated. The main scientific-research institute on the problem of improving asphalt production — Bashkir Scientific-Research Institute of the Petroleum Industry — at one time preferred the tubular reactor [41].

For this reason, design organizations — the Rostov and Omsk branches of the All-Russian Petroleum Scientific Research and Planning Institute — developed designs for large-capacity asphalt units using tubular reactors as oxidizing vessels. Six units were constructed in the 1970s and five units were planned to begin operation during the Five Year Plan; in addition, plans for a number of refineries were drawn up.

Tubular reactors [41] were selected because the asphalts produced in these reactors with the same feedstock had a slightly higher softening point than asphalts with the same penetration at 25°C produced in a column. This allowed considering the possible use of heavier vacuum resid as oxidation feedstock and attaining a higher degree of takeoff of vacuum distillates.

However, the experience of the **Novopolotsk** and **Kirishi** refineries showed that there is no significant difference in the properties of asphalts produced in tubular reactors and columns [42, 43]. This difference is only manifested in comparatively deep oxidation of light vacuum resids into construction asphalts, for example [1], but is of no practical importance.

In addition, the drawbacks of the oxidation process in tubular reactors — high power consumption (for recirculation of asphalt, compression of air to higher pressures, heating of feedstock, and cooling of the reactor), coking of the evaporators and reactors, more complicated regulation — have become increasingly evident. All of this led to a re-assessment of the efficiency of the different oxidizing vessels: in the mid-1970s, approximately 30% of oxidized asphalts were produced in columns [44] and only 13% in tubular reactors [45].

Unfortunately, the main factor that affected the predominant use of columns was not the reduction in power consumption (which was not attributed great importance at that time) but the change in feedstock quality. In these years, many plants in the country began to use West Siberian crude, and the proportion in the mixed crudes constantly increased. This also affected the feedstock for asphalt production.

The viscosity of vacuum resids and asphalts became much lower than for vacuum resids and asphalts from Romashkino or Volgograd crudes [46 - 49], which required operatively making up for the shortage of oxidizing capacities for processing the previous assortment of asphalts. This problem was easily solved by installing columns, where the cylindrical vessels available in the refineries were used as such columns.

In domestic practice, the initial period of use of columns is to a great degree related to the work of **R. B. Gun** [5]. Then vessels from other units were installed in operating asphalt plants so that the column size varied within wide limits: the diameter from 2.2 to 3.8 m and the height from 10 to 30 m [1]. Due to the lack of well-founded recommendations, selection of the sizes was random and the columns were only used for preliminary oxidation of the feedstock.

The tests performed at the Angarsk Refinery by specialists from I. M. Gubkin Moscow Institute of the Petrochemical and Gas Industry, Bashkir Scientific-Research Institute of the Petroleum Industry, and the Rostov branch of the All-Russian Petroleum Scientific-Research and Planning Institute were an important stage in the development of column oxidation technology [50]. The possibility of producing different brands of paving and construction asphalts from West Siberian crude vacuum resid delivered to most of the country's refineries was demonstrated. The specific air flow rates for production of different brands of asphalt were established.

The results obtained were used in designing columns for the asphalt units in other refineries. However,

according to the data in [5, 50], when the column air load was increased in the range of $2.4 - 3.9 \text{ m}^3/(\text{m}^2 \cdot \text{min})$, the degree of oxygen utilization decreased so that this load did not exceed $4 \text{ m}^3/(\text{m}^2 \cdot \text{min})$ in practice [44, 46], only occasionally attaining $5 \text{ m}^3/(\text{m}^2 \cdot \text{min})$ [42].

This prevented intensifying the regime and limited the productivity of the columns. To increase it, columns of larger diameter were provided in the designs for new asphalt plants: up to 3.6 [51] and 3.8 m [52].

The restriction on column productivity and the lower efficiency of utilization of atmospheric oxygen in them than in tubular reactors in production of construction asphalts remained the basis for use of tubular reactors. The results of the tests at **Kirishi Refinery** became the decisive premise for almost universally changing to oxidation in columns.

We performed these tests and took the deliberate risk which perturbed the operational restrictions on air feed noted above. It was found that the air load for the column can be increased significantly without decreasing the degree of atmospheric oxygen utilization: at least to 8 and 16 m³/(m²·min) for construction [53] and paving [54] asphalts, respectively.

The results of pilot industrial runs of oxidizing columns at Novopolotsk and Syzran' Refineries also indicate the possibility of attaining a high degree of oxygen utilization with high air loads; approximately $8 \text{ m}^3/(\text{m}^2 \cdot \text{min})$. In all of these cases, ordinary dispersers with openings 8 - 18 mm in diameter were used.

What is the cause of the inaccurate evaluation of the effect of increasing the air flow rate in the column on absorption of oxygen in [50]?

The analysis of the primary experimental material used in this study showed: the concentration of atmospheric oxygen in the oxidation gases is actually higher (and the degree of oxygen utilization in oxidation reactions is correspondingly lower) with a high air flow rate.

However, the difference in the results of determining the oxygen content for different air flow rates is within the limits of the accuracy of the method used, as noted in [1]. In addition, runs with high air loads were conducted by workers in one shift and runs with low loads were conducted by workers from another shift. This could be a source of systematic error in determining the oxygen content in oxidation gases.

The possibility of increasing the productivity of existing columns by increasing the air feed or decreasing the diameter of the reaction section while preserving the productivity was thus substantiated. This was one of the factors responsible for failure of the tendency to increase the column size.

Three other important observations that affected the principle of improving the column as an oxidizing vessel were made during the pilot-industrial runs at **Kirishi Refinery** [53, 54]:

• entrainment of asphalt (in the form of drops) from the separation section to the wash pipe is a function of the air flow rate. To eliminate entrainment, limiting the gas load in the separation section to a value of $5 \text{ m}^3/(\text{m}^2 \cdot \text{min})$ was proposed. By using this value, it is possible to calculate the section area and consequently separation section diameter in designing new columns;

• air dividers had no serious effect on improving oxygen absorption so that the design of this type of column does not have to be complicated by internal devices;

• the degree of atmospheric oxygen utilization in production of construction asphalts increases significantly with an increase in the oxidation temperature to 290° C. Their quality satisfies the requirements of the standard; however, increasing the oxidation temperature is unavoidably accompanied by an increase in the temperature at the top of the column — to a value where the temperature begins to rise uncontrollably (due to "burning" of hydrocarbon vapors or coke deposits); to suppress this increase, it is necessary to feed an inert gas into the column's gas space, which requires additional outlays.

The pilot-industrial run at Novo-Ufimskii Refinery also showed a significant increase in the degree of atmospheric oxygen utilization when the oxidation temperature was increased to 290° C. The properties of the construction asphalts obtained were almost identical to the properties of the asphalts obtained at 270° C [44].

Based on the data obtained, a new method of conducting column oxidation was proposed; it ensures fire safety and a high degree of atmospheric oxygen utilization in production of both paving and construction asphalts [1]. The essence of this method consists of design separation of the reaction and separation sections and cooling the gas-liquid mixture going from the reaction section to the separation section with the feedstock. The feedstock initially goes to the separation section and is then delivered to the reaction section with the recirculated substance by overflow. Different temperatures are maintained along the height of the liquid phase in the column due to the separating device reorganized by movement of the gas and liquid phase streams and quenching by the feedstock: in the reaction section — relatively high, ensuring almost total utilization of atmospheric oxygen; in the separation section — low, eliminating coking of the gas space.

A design for a two-section oxidizing column was drawn up based on a proposal by **Bashkir** Scientific-Research Institute of the Petroleum Industry and Rostgiproneftekhim. However, the practical use of this proposal was delayed because of various organizational difficulties so that attempts were made to implement the design in operating asphalt units using existing equipment.

An important role in the successful introduction of oxidation in a column with a quenching section must be attributed to A. I. Samokhvalov; the fundamental technical solutions were tested at the Moscow Refinery [55] and then this process as a whole was used for the first time [1]. Columns with quenching sections were later introduced at Ryazan' [49] and Pavlodar Refineries [1, 56].

The use of these columns allows reducing the air consumption for oxidation and the fuel consumption for thermal decontamination of gases by approximately 1.5 times, i.e., decreasing the power consumption and atmospheric emission of harmful substances.

At present, different designs of oxidizing columns with quenching sections are successfully operating at most asphalt plants. The processability [49] and ease of assimilation [56] of the proposed version of the process were noted from the time of introduction by representatives of the refineries.

However, introduction without involving the developers was not error-free. The buoyancy force acting on the separating device was not taken into consideration at **Kirishi Refinery**. The oxidizing columns at **Pavlodar Refinery** and the new asphalt unit at **Moscow Refinery** were too large; no mathematical model of the oxidation process which would allow substantiated calculation of their size was developed; the bureaucratic procedures in the design, dimensioning, ordering, and equipment preparation stages were too long.

It was attempted to implement the frequently proposed oxidation principle in existing equipment, for example, by repiping. This prevented obtaining the optimum result but confirmed the possibility of successfully introducing the new technology in unfavorable conditions.

The 20 years of experience in utilizing columns with a quenching section for oxidizing different feedstock and obtaining a wide assortment of asphalts (roofing, paving, and construction) with a softening point up to 100° C [1, 11, 49, 57, 58] will allow finding the optimum solution of the problems that arise in refineries.

To increase the duration of operation of columns with a quenching section, **Bashkir Scientific-Research Institute of the Petroleum Industry** proposed fitting them out with a separating partition separating the air dispersion section. Maintaining a low temperature in this section (by analogy with the separation section) is an addition measure for preventing coking of the disperser; continuous operation of the column itself is, as noted above, an effective method of preventing coking.

Three-section columns are being used at **Mazheisk** [59] and **Moscow Refineries**. A successful solution which eliminates coking of the disperser is being used at **Perm' Refinery**: air is introduced in the column through the end holes of horizontal pipes up to 80 mm in diameter; large air bubbles are broken up by colliding with angle irons installed opposite the holes.

The technical and economic indexes of oxidation in a column with a quenching section are higher than the corresponding indexes characteristic of other oxidizing vessels used in some refineries of the former USSR. The PORNER (Australia) reactor is easy to control, but is equipped with a motor which utilizes a significant amount of electric power to attain such a high degree of utilization of atmospheric oxygen. MAG Grimma (Germany) proposes using a column with a quenching section in the rebuilt asphalt unit at Ukhta Refinery.

The problem of creating an efficient oxidizing vessel for asphalt plants can thus be considered solved.

REFERENCES

- 1. I. B. Grudnikov, Production of Petroleum Asphalts [in Russian], Khimiya, Moscow (1983).
- 2. I. B. Grudnikov, in: Fuels, Lubricants, Industrial Fluids [in Russian], Tekhinform, Moscow (1999), pp. 491 498.
- 3. A. S. Kolbanovskaya and V. V. Mikhailov, Paving Asphalts [in Russian], Transport, Moscow (1973).
- 4. V. V. Fryazinov and R. S. Akhmetova, Trudy BashNII NP, 8, 167 170 (1968).

- 5. R. B. Gun, Petroleum Asphalts [in Russian], Khimiya, Moscow (1973).
- 6. S. A. Apostolov, Scientific Principles of Asphalt Production [in Russian], LGU, Leningrad (1988).
- 7. I. B. Grudnikov and V. V. Fryazinov, Neftepererab. Neftekhim., No. 8, 8 9 (1971).
- L. N. Shabalina, M. A. Drozdova, V. S. Kogan, L. Ya. Vlasenko, N. I. Mel'nik, and N. P. Pankov, *Ibid.*, No. 5, 12 - 14 (1980).
- 9. N. Ya. Rudakova, A. V. Timoshina, Z. V. Kocheva, A. D. Bilonizhko, F. Kh. Sharf, and A. Ya. Koldovkin, *Ibid.*, No. 6, 11 13 (1978).
- 10. I. B. Grudnikov, Khim. Tekhnol. Topl. Masel, No. 12, 16 18 (1976).
- 11. I. R. Kazo and I. B. Grudnikov, Ibid., No. 11, 18 (1988).
- 12. R. Kh. Salimgareev, B. N. Davydov, E. V. Lutset, and E. K. Poletaeva, Ibid., No. 5, 17 19 (1991).
- 13. V. V. Fryazinov, R. S. Akhmetova, and I. B. Grudnikov, Neftepererab. Neftekhim., No. 8, 14 16 (1967).
- V. V. Fryazinov, R. S. Akhmetova, I. A. Chernobrivenko, M. Sh. Yamaeva, and N. G. Stepanova, *Ibid.*, No. 7, 2 - 7 (1977).
- 15. I. B. Grudnikov and M. Sh. Yamaeva, Trudy BashNII NP, 20, 38 43 (1981).
- R. S. Akhmetova, A. M. Baimbetov, A. K. Syunyakov, R. F. Sharafutdinov, and N. G. Stepanova, Neftepererab. Neftekhim., No. 6, 10 - 11 (1981).
- 17. S. A. Zaitseva and M. Sh. Yamaeva, Khim. Tekhnol. Topl. Masel, No. 6, 40 44 (1987).
- 18. V. V. Fryazinov, R. S. Akhmetova, I. A. Chernobrivenko, and R. Kh. Salimgareev, *Ibid.*, No. 6, 17 20 (1981).
- 19. T. S. Khudyakova, V. V. Gur'yanov, M. A. Zheleznikov, and M. S. Mokhovoi, *Ibid.*, No. 2, 6 8 (1995).
- 20. G. A. Popandopulo, Avtomobil. Dorogi, No. 8, 24 (1990).
- 21. G. N. Kiryukhin, *Ibid.*, No. 5, 3 4 (1991).
- 22. B. G. Pechenyi, Asphalts and Asphalt Composites [in Russian], Khimiya, Moscow (1990).
- 23. A. V. Rudenskii, Asphalt Concrete Pavements [in Russian], Transport, Moscow (1992).
- 24. M. A. Zheleznikov, Avtomobil. Dorogi, No. 6, 44 45 (1999).
- 25. T. S. Khudyakova, *Ibid.*, No. 9, 40 41 (1996).
- 26. L. M. Gokhman and E. M. Gurarii, *Ibid.*, No. 3, 12 13 (1997).
- 27. V. N. Chistyakov, N. V. Parygina, V. V. Kolesov, and V. G. Lyuosev, Ibid., No. 6.
- Yu. A. Kut'in, I. R. Khairudinov, S. S. Mingaraev, and I. Kh. Gaisin, Neftepererab. Neftekhim., No. 9, 20 24 (1998).
- 29. A. F. Ishkil'din, S. L. Aleksandrova, and S. S. Mingaraev, Khim. Tekhnol. Topl. Masel, No. 1, 17 (1997).
- 30. S. L. Aleksandrova, V. V. Taushev, G. G. Valyavin, L. B. Kudaidatova, and S. S. Mingaraev, Neftepererab. Neftekhim., No. 5, 14 18 (1997).
- 31. I. B. Grudnikov, in: Petroleum Refining Handbook [in Russian], Khimiya, Leningrad (1986), p. 296.
- 32. V. M. Shkol'nikov and I. O. Kolesnik, *Ibid.*, p. 206.
- 33. A. D. Rozental', V. E. Somov, A. M. Syroezhko, and I. N. Kudryavtseva, Zh. Prikl. Khim., 71, No. 8, 1405 1407 (1998).
- 34. E. V. Ippolitov, N. P. Fedyanin, and I. B. Grudnikov, Neftepererab. Neftekhim., No. 7, 24 27 (1998).
- 35. T. Blumberg and O. Popov, Avtomobil. Dorogi, No. 1, 11 13 (1999).
- 36. V. V. Fryazinov, R. S. Akhmetova, and L. V. Evdokimova, Neftepererab. Neftekhim., No. 9, 11 14 (1979).
- L. S. Tabolina, V. Yu. Bazhenov, I. N. Kudryavtseva, D. A. Rozental', and L. I. Khromova, *Ibid.*, No. 4, 7-9 (1987).
- 38. N. A. Panin and I. G. Nakipova, *Ibid.*, No. 5, 10 11 (1989).
- 39. A. I. Snegur and A. A. Kruglov, *Ibid.*, No. 1, 8 9 (1985).
- 40. V. V. Fryazinov, R. S. Akhmetova, and I. B. Grudnikov, *Ibid.*, No. 10, 41 44 (1977).
- 41. V. V. Fryazinov, V. N. Pikalov, R. S. Akhmetova, and R. Kh. Salimgareev, *Trudy BashNII NP*, 11, 101 110 (1973).

- 42. P. I. Korotkov, A. D. Rudkovskii, V. S. Kechko, N. I. Milosh, V. M. Kadunin, and G. A. Lysakov, *Neftepererab. Neftekhim.*, No. 1, 11 13 (1977).
- 43. Yu. A. Egorov and E. V. Ippolitov, *Ibid.*, No. 7, 1 2.
- 44. I. B. Grudnikov and V. V. Fryazinov, Khim. Tekhnol. Topl. Masel, No. 8, 8 12 (1978).
- 45. V. V. Fryazinov and I. B. Grudnikov, *Ibid.*, No. 2, 11 14.
- 46. R. S. Akhmetova, N. G. Stepanova, L. V. Evdokimova, and I. A. Chernobrivenko, *Ibid.*, No. 2, 10 12 (1979).
- 47. V. D. Egorov, V. V. Shelikhov, L. A. Podlesnaya, M. A. Lomovtseva, L. A. Vakhtina, and M. N. Sidyakin, *Neftepererab. Neftekhim.*, No. 6, 27 - 29 (1979).
- 48. A. I. Snegur and N. A. Panin, *Ibid.*, No. 11, 3 5 (1984).
- 49. V. I. Abramov, *Ibid.*, No. 9, 18 20 (1985).
- A. I. Levin, R. B. Gun, V. V. Fryazinov, R. S. Akhmetova, V. N. Pikalov, M. A. Budnik, K. N. Fattakhov, N. G. Stepanova, N. P. Mazin, I. N. Likhter, N. N. Belyi, and V. A. Kuz'min, *Khim. Tekhnol. Topl. Masel*, No. 3, 46 - 49 (1973).
- 51. V. K. Aleksandrov, I. A. Azarov, V. D. Lugovskoi, R. Yu. Askerzade, and E. L. Guseinov, Neftepererab. Neftekhim., No. 5, 9 11 (1974).
- 52. A. F. Kekukh, N. N. Belyi, Yu. V. Makhrov, and I. E. Bogdanov, Khim. Tekhnol. Topl. Masel, No. 2, 20 22 (1975).
- 53. P. G. Bannov, V. V. Fryazinov, I. B. Grudnikov, Yu. A. Egorov, and E. V. Ippolitov, Neftepererab. Neftekhim., No. 9, 14 16 (1977).
- 54. L. G. Bannov, V. V. Fryazinov, I. B. Grudnikov, Yu. A. Egorov, M. A. Borisov, and E. V. Ippolitov, *Ibid.*, No. 9, 12 14 (1978).
- 55. A. I. Samokhvalov, I. B. Grudnikov, V. V. Fryazinov, L. N. Shabalina, N. P. Pankov, and G. A. Vorms, *Ibid.*, No. 4, 9 11 (1981).
- 56. V. P. Sidorin, S. A. Vol'fson, B. I. Kryvelev, V. M. Tomilin, and G. I. Glazov, *Khim. Tekhnol. Topl. Masel*, No. 5, 7 – 8 (1982).
- 57. A. A. Kas'yanov, A. M. Sukhorukov, S. A. D'yachenko, I. B. Grudnikov, N. S. Kuznetsova, and S. G. Prokopyuk, *Ibid.*, No. 4, 25 26 (1999).
- 58. I. B. Grudnikov, I. V. Egorov, and S. G. Prokopyuk, Neftepererab. Neftekhim., No. 5, 42 45 (1999).
- 59. L. Sh. Vilenskii, L. V. Aleksandrova, and V. A. Kozlov, *Ibid.*, No. 10, 5 8 (1990).