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NATURAL ASPHALTS – PROPERTIES AND USE [1]

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The article describes and illustrates natural asphalts according to the classification due to the solubility of carbon disulphide. The review of bitumens and the sources of their acquisition aims to systematize knowledge on this subject in terms of practical application. Exemplary applications on an industrial scale, discussed natural asphalts with particular emphasis on their use in road construction have been presented.

1. INTRODUCTION

The term "asphalt" (bitumen) is used both in the description of artificial asphalt obtained in petroleum processing (the so-called petroleum bitumen, refined bitumen), as well as the raw resources in form of natural deposits. Natural asphalt is composed of organic and mineral substances with water [1]. The organic part is a compound mixture of hydrocarbons, asphaltites and resins, accompanied by considerable amounts of sulphur, oxygen, nitrogen, as well as vanadium, nickel and iron in its carbon structure [2]. Following the definition provided in the EN 12597 standard [3], natural asphalt is relatively hard, can be found in natural deposits, and is often mixed with fine or very fine mineral material, which usually appears in solid form in the temperature of 25°C, and as viscous liquid in 175°C.

2. CLASSIFICATION AND USE OF NATURAL ASPHALTS

The primary method for classifying natural asphalts is their ability to dissolve in CS_2 (carbon disulphide) [2, 4]. Fig. 1 shows a classification of natural asphalts in relation to their solubility in CS_2, and provides examples of deposits or names of minerals they can be found in.

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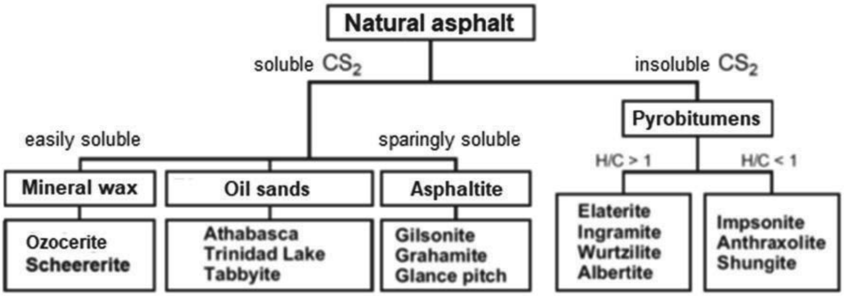

Fig. 1. Classification of natural asphalts (prepared based on [2, 4])

2.1. Pyrobitumens

Pyrobitumens are a group of natural asphalts insoluble in carbon disulphide CS_2 (Fig. 2), which are classified according to the ratio of the content of hydrogen atoms to carbon (H/C), i.e. whether it is larger or smaller than one. The group of pyrobitumens, in which the amount of hydrogen atoms is larger than that of carbon atoms, comprises e.g. the mineral elaterite (Fig. 3), which is a dark brown elastic hydrocarbon often called elastic bitumen (asphalt) or mineral rubber [5]. The second group, on the other hand, includes e.g. impsonite with a carbon content of 50% to 85%, which arises from liquid bitumen (asphalt) in the polymerization process after filling the vein in the geological layer [6].

Fig. 2. Photography of pyrobitumen extracted from a diabase quarry in Tegau-Schleiz (Thuringia, Germany), *source: www.mindat.org/photo-157434.html*

In general, pyrobitumen is a material occurring in nature as an insoluble mineral, in most carbonate deposits taking the form of a black, solid mineral comprised of non-volatile components. Due to their chemical composition, they block the permeability of reservoir rocks (closing of pore spaces), which means that the presence of pyrobitumens is not favourable when hydrocarbons such as, for example, petroleum, are to be extracted [7].

Fig. 3. Photography of elaterite extracted in Matlock (England, UK), *source: www.mindat.org/photo-278021.html*

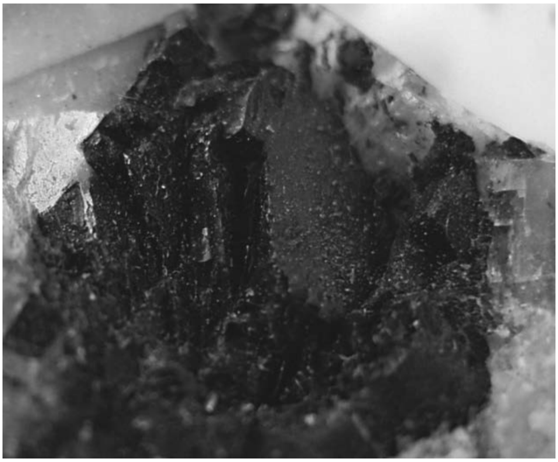

Fig. 4. Photography of impsonite extracted in the region of Murmansk on the Kola Peninsula (Russia), *source: www.mindat.org/photo-34116.html*

Pyrobitumens are used as sealing compounds, a control rods component, and in nuclear reactors or in the production of black pigments [8]. However, they are not applied in road engineering in the role of bitumen modifiers used in hot mix asphalt. The facilities in which pyrobitumens are extracted at the industrial scale are located, among others, in the state of Utah (USA), Argentina or China [8]. Pyrobitumens occur in nature prevailingly as veins and bedded deposits (strata created in magmatic processes in the continental crust environments [9]).

They can be also produced in the course of industrial processes, e.g. in the last stage of thermal cracking of oils and their surface degradation [8].

2.2. Mineral wax

Natural asphalts easily soluble in CS_2 carbon disulphide include mineral wax. They resemble pyrobitumens very much in terms of their physical characteristics, with a ratio of hydrogen atoms to carbon greater than one; however, they differ from them with respect to their solubility in CS_2 due to the presence of paraffin and cycloalkanes in their composition. These minerals include ozocerite (Fig. 5), which is easily melted and consists almost exclusively of paraffin [2]. The most well-known ozocerite deposits are located in the Ukraine, in the neighbourhood of Boryslav. In the past, ozocerite referred to as “earth wax” was applied for industrial production of ceresin, used among others in the production of candles, synthetic waxes and pastes [10]. In the modern times, ceresin, i.e. refined ozocerite, is derived from residues of petroleum processing [11]. Scheererite is the local name for ozocerite found in the area of St. Gallen (Switzerland), which features a slight gloss and a white to dark yellow colour and is formed of crystalline grains or thin layers in brown coal deposits [12, 13]. Due to the stiffening properties arising as part of their ageing processes, synthetic or natural paraffin additives are rarely used as road bitumen modifiers [14].

Fig. 5. Photography of ozocerite exploited in the Soldier Summit mountain pass (Utah, USA), *source: www.mindat.org/photo-319575.htm*

2.3. Oil sands

The term “oil sands” or “tar sands” (the last name is disputed in the English-language publications as far as its matter-related correctness is concerned) means rocks consisting of a very viscous mixture of hydrocarbons, which cannot be recovered in their natural state by means of drilling a conventional oil well. Sandstone or limestone deposits are usually reservoirs for heavy crude oil in solid or almost solid form. Natural bitumen is either a consolidated material with sandstone (limestone), sometimes referred to as asphalt rocks, or it fills free spaces in it and can migrate to the surface over time. The process of recovering natural bitumen depends to a large extent on the composition of oil sands and usually requires the use of high temperatures to separate individual components. Due to the great difficulties associated with obtaining pure natural bitumen and a very high diversity of oil sands, many deposits are not industrially used [4, 15]. The most well-known oil sands deposits are [1]:

- Athabaska (Canada),
- Bermudez Pitch Lake (Venezuela),
- Selenizza (Albania),
- Trinidad Pitch Lake (Trinidad and Tobago),
- Tabbyite (USA).

Many other smaller deposits are located in the areas of, among others, Middle East, e.g. Syria, Iraq, the bed of the Dead Sea.

Oil sand deposits in Athabasca (Fig. 6) are located in the neighbourhood of Fort McMurray in the north part of the Alberta province in Canada; their name stems from the river flowing through the area. Athabasca oil sands consist of sand (up to 83%), natural binder (from 10% to 20%), water (4%) and clay (3%). Their origin is associated with tectonic movements and formation of sedimentary rocks in Cretaceous. Natural binder is obtained at the industrial scale by use of Hot Water Extraction (enormous energy is required) to separate the binder from other components. Due to the fact that the obtained natural binder is poor in hydrogen, it is subjected to further technological processes (coking, distillation, catalytic conversion and hydrotreating) in order to obtain a more valuable material, in effect similar to crude oil, which can be further industrialised [4].

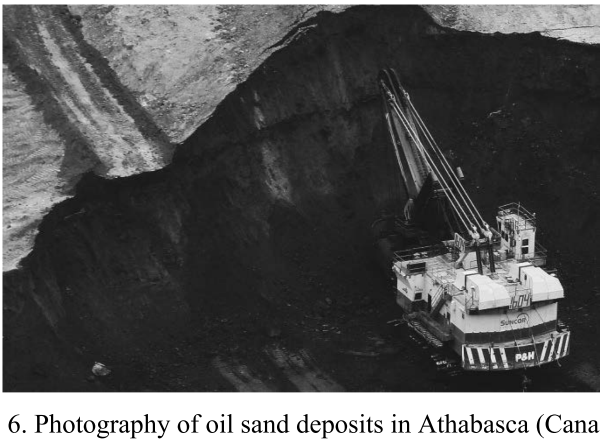

Fig. 6. Photography of oil sand deposits in Athabasca (Canada), *source: Suncor Energy Inc.*

Oil sand deposits in the form of so-called Bermudez and Trinidad asphalt lakes (Pitch Lake) are very similar to each other, as a result of a relatively small distance between them (Fig. 7).

Fig. 7. Photography of the Trinidad Pitch Lake asphalt lake (Trinidad and Tobago), *source: www.panoramio.com/photo/75896867*

In most general scientific publications, they are usually called natural asphalts. The Bermudez deposit is located near the river mouth of the Orinoco River to the Atlantic Ocean in North-Eastern Venezuela, and Trinidad near the town of La Brea on the island of Trinidad [4]. In the case of the Bermudez deposit, the naturally occurring raw material may contain from 5% to 30% of bitumen (asphalt) of varying hardness (the rest being usually sandstone or limestone), which means that this material is not obtained for industrial purposes [17]. On the other hand, the raw material from the Trinidad Pitch Lake deposit is exploited at the industrial scale. The natural asphalt recovered from the surface of the lake is subjected to the refining process in order to soften it, evaporate free water and chemical compounds dissolved in it, as well as to separate mineral and organic impurities, e.g. in the form of stones or wood. The application of this technology makes it possible to obtain a product called purified asphalt, known as Epuré or Trinidad Epuré (TE). The content of the components in the material obtained in the refining process in relation to its mass is as follows: natural binder - from 53% to 55%, mineral dust - from 36% to 37%, ashes - from 9% to 10%. Trinidad Epuré is most often used in road engineering to modify bitumen applied in hot mix asphalt [18]. The benefits of using in hot mix asphalt the Trinidad Epuré (TE) asphalt additives, also referred to in publications as Trinidad Lake Asphalt (TLA), have been scientifically proven. Based on the tests [19, 20, 21, 22] related to the modification of Trinidad Epuré road bitumen additive it was possible to observe a decrease in the penetration value, an increase in the softening temperature value, an increase in resistance to permanent deformations at high temperatures - increase of the $G^{*}/\sin(\delta)$ parameter. In the case of road pavements made of a hot mix asphalt prepared with the use of an asphalt binder with the Trinidad Epuré additive, an improvement in the workability and compactability of the hot mix asphalt was observed [23]. In Germany, the asphalt Trinidad Epuré additive is successfully used in the so-called hot thin wearing courses or as an additive in hot mix asphalt type mastic asphalt (MA) [24].

Oil sands in the Selenizza deposit located near Selenice in Albania are the source of a material with a high natural binder content - over 80% (Fig. 8).

Fig. 8. Photography of crushed oil sands of Selenizza (Albania),
source: www.selenizza.eu

In terms of its chemical composition, this raw material highly resembles asphaltite (in some papers it is even counted as one of the asphaltites). The deposits were created during the Pliocene as a result of Miocenic sand beds becoming saturated with petroleum. This raw material is successfully applied as an additive to oil-derived asphalts. The hot mix asphalt made using the Selenizza oil sand feature similar properties to mixtures containing the natural Trinidad Epuré asphalt [4, 25].

Oil sands found in the state of Utah in the US are known as *tabbyite*. In terms of their visual appearance, they are similar to oils sands from Selenizza (Fig. 9). In the state of Utah, besides *tabbyite*, there are many natural hydrocarbon deposits, such as ozokerite, gilsonite, wurtzilite or petroleum [4]. In total, there are about 15 different hydrocarbons in Utah, ranging from insoluble in carbon disulphide, like wurtzilite, to easily soluble, such as ozocerite [26].

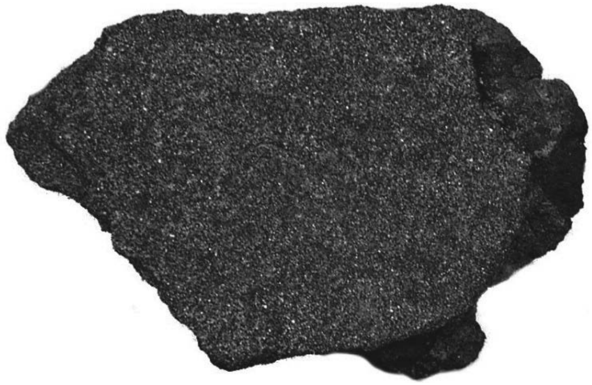

Fig. 9. Photography of oil sand extracted from the Asphalt Ridge deposit in Vernal (Utah, USA), *source: www.ostseis.anl.gov/guide/photos/index.cfm*

2.4. Asphaltites

Asphaltites belong to the group of raw materials that are sparingly soluble in CS_2 carbon disulphide. They are glossy, black, solid hydrocarbons, which resemble hard coal with regard to their visual appearance. They can be found all around the world under various names due to very slight differences in their chemical composition. Grahamite deposits can be found in Cuba, Mexico and the United States, while Glance pitch deposits are encountered in Barbados and Colombia [27]. Iran is the home of asphaltite deposits called Iranian natural bitumen (Iranian Gilsonite) [28]. The most well-known mineral in the group of asphaltites, however, is Gilsonite (Fig. 10). It owes its name to Samuel H. Gilson, who was one of its discoverers and promoters as, among others, a sealing material.

Fig. 10. Photography of uintahite mineral (Gilsonite) extracted in the Fort Duchesne mine (Utah, USA), *source: www.mindat.org/photo-12288.html*

Gilsonite deposits are located in the north-eastern part of the state of Utah (USA), in the Green River river bed, deep beneath the Uintah basin, hence in scientific studies this mineral also occurs under the name of uintahite. Due to its registered trademark, however, this ore can usually be encountered under the name Gilsonite. This material is a natural mixture of (per product mass) coal - 85%, hydrogen - 10%, nitrogen - 3% and oxygen, sulphur and other components in the amount of about 2%. The genesis of Gilsonite deposits is related to the kerogen, the so-called immature petroleum, as under the conditions of high pressure and temperature kerogen transforms into crude oil [27, 29, 30]. After being crushed, it is delivered to customers in from of a granule with a grain size of 0/2 mm or powdered [31]. Gilsonite is used as a component of drilling fluids, inks, various chemical products or as an additive to metallurgical castings and, of course, oil-derived asphalts [29].

Due to its origins, chemical composition and high molecular mass, Gilsonite is well related to asphalt. Applying this additive for oil-derived asphalt modifications reduces the penetration values and increases the values of softening temperatures of asphalt binders containing Gilsonite [20]. The Gilsonite additive increases resistance to permanent deformations at high temperatures, and also increases the $G^{*}/\sin(\delta)$ parameter of asphalt binders modified with this additive before and after the ageing process. Hot mix asphalt modified with the Gilsonite additive are characterized by increased stability and a lower range of permanent deformations, which translates into a higher resistance to rutting while unimpaired resistance to fatigue cracking and low temperature cracking is retained [32, 33, 34].

Smaller asphaltite deposits are located in the United States in the states of Alabama, California, Colorado, Kentucky, Oklahoma, Teksas, and of course Utah. In Europe, asphaltites have been encountered in Seyssel in France, Ragusa in Sicily, Val-de-Travers in Switzerland, and Vorwhole in Germany [35].

3. SUMMARY

This article provides a concise overview of natural asphalts, both those which are not industrially used, and those finding application in various branches of economy. Some of the natural asphalts, such as e.g. oil (bituminous) sands can be used as a source of "alternative petroleum". On the other hand, natural asphalts such as Trinidad Epuré or Gilsonite are successfully used as bitumen (asphalt) modifiers applied in hot mix asphalt. Due to varying methods of creation (origin), and different carbon and hydrogen content, it is possible to distinguish several groups of natural asphalts. Because of minor differences in the chemical composition of particular natural asphalts, they can be encountered all around the world under various names. In short, the term 'natural asphalts' (asphalt rocks) can be applied to an array of hydrocarbonic raw materials and minerals found in nature.

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ASFALTY NATURALNE – CHARAKTERYSTYKA I ZASTOSOWANIE

Streszczenie

W artykule zostały scharakteryzowane i zilustrowane asfalty naturalne według klasyfikacji ze względu na rozpuszczalność w dwusiarczku węgla. Przegląd asfaltów i źródeł ich pozyskiwania ma na celu usystematyzowanie wiedzy na ten temat pod kątem możliwości zastosowania praktycznego. Przedstawiono przykładowe zastosowania w skali przemysłowej omawiany asfaltów naturalnych ze szczególnym uwzględnieniem ich wykorzystywania w budownictwie drogowym.

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