Chapter 5
Oil Shales

Keywords Homogeneous mixtures · Inorganic materials · Organic materials · Oil shales · Ölschiefer · Burning shales · Bituminous · Oil shale deposits · Lakes · Shallow seas · Organic-mineral complexes · Immature kerogen · Bitumen · Mineral materials · Silicates · Carbonates · Pyrite · Kerogen · Bitumen · Pyrolysis · Synthetic oil · Semicoke · Gaseous products · Fischer retort

Outline

Oil shales have always attracted attention as a source of energy and industrial raw materials and in recent time as a very interesting substrate in fundamental organic-geochemical studies. Definition and oil shale terminology, organic geochemistry of oil shales, composition (inorganic and organic parts) and usage of oil shales will be discussed here in more detail.

5.1 Definition and Terminology

According to the most general definition, oil shales are clayey-marley-carbonate sedimentary rocks, with more or less organic matter content. Oil shales are homogeneous mixtures of inorganic and organic materials. They are widespread distributed but differ enormously with respect to inorganic and organic fractions, as well as their complex and variable composition. For this type of sedimentary rocks there is no suitable geological or chemical definition, but it is usually based on the economic-technical explanation.

However, all oil shales have the following common features that can be incorporated into a more detailed definition:

a. at dry distillation, i.e. when heated without access of air (pyrolysis), the main useful product is crude oil of hydrocarbon composition (once referred to as tar, and nowadays as synthetic oil);
b. most of the organic matter of oil shales occur in the form of kerogen, and is not soluble in organic and inorganic solvents; and
c. the content of mineral substances is usually very large.

J. Schwarzbauer, B. Jovančićević, *Fossil Matter in the Geosphere,*
Fundamentals in Organic Geochemistry, DOI 10.1007/978-3-319-11938-0_5

The term oil shale corresponds to the French, “schiste bitumineux” and to the German the “Ölschiefer”. In Russian oil shales are called “горючиесланцы” (“burning shales”). Sometimes the English term “bituminous” shale is used.

Box 5.1: *General Note*

The term oil shale may mislead those who are not professionals in this area, suggesting that it is maybe an oil-impregnated rock. This, however, is not the case because most of its organic matter is in the form of insoluble kerogen from which oil can be extracted only by thermal processing. It happened that even experts have a wrong idea of the “oil shale”, believing that, since they are “oil-impregnated”, it is possible to easily separate organic matter from mineral admixtures by simple extraction.

5.2 Conditions for the Formation of Oil Shale Deposits—Organic Geochemistry of Oil Shales

Oil shales are formed during more than 500 million years in almost all geological periods (Fig. 5.1). Oil shale deposits have usually been formed:

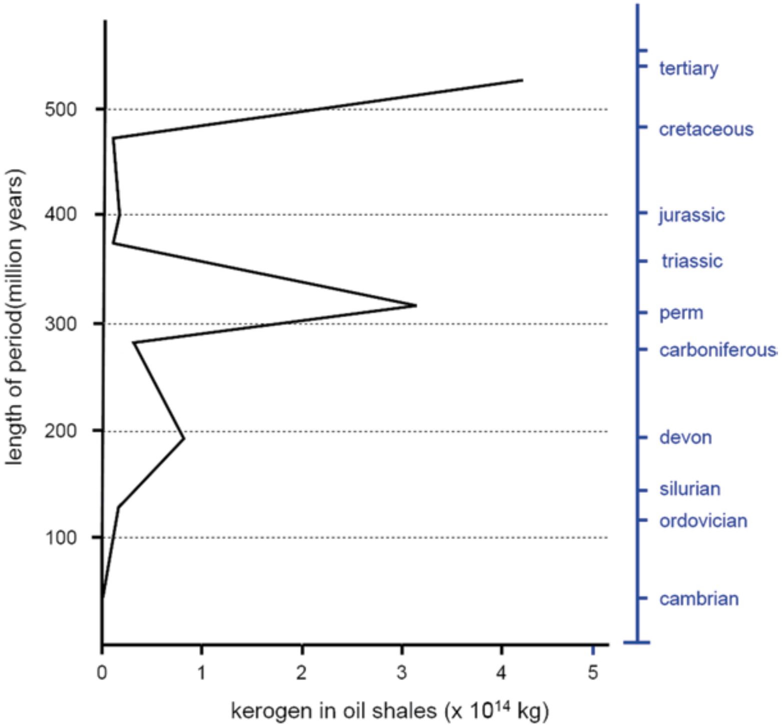


Fig. 5.1 Oil shale deposits in different geological periods

- in large lakes, particularly those that were formed during the formation of mountains; mineral part of these shales is marly or clayey-carbonate;
- in shallow seas, where they formed a relatively thin layer several centimetres (or meters) to several tens of meters thick, but in a very large area; in this case the mineral part is mainly composed of silicon dioxide and clay, and possibly carbonates; and
- in small lakes, swamps, lagoons and flooded areas where coal strata have also been formed, so that the shale deposits often occur in the overlying or underlying coal beds.

Typical characteristic of oil shales is a fine stratification with alternating layers of mixed organic and mineral material (organic-mineral complexes) and pure mineral material. Stratification indicates calm sedimentary conditions in which the minerals are precipitated from solution (carbonates) or are applied in the form of very fine particles (e.g. clay minerals) and alternate seasonal deposition. The deposits and reservoirs of oil shales are mostly superficial or shallow. Their kerogen, regardless of the age of sediment, is usually immature, but the layers of shale may be found at greater depths at which the source rocks for oil are formed.

Based on the composition and structure of kerogen of oil shales, and in particular on the basis of biological markers in the corresponding bitumen, it is possible to link the organic matter with biolipids of flora and fauna, plant and animal precursors, and thus to explain the origin of sediments, depositional conditions, diagenetic and possibly other transformations.

5.3 Composition of Oil Shales

The composition of oil shales is schematically shown in Table 5.1.

5.3.1 *Inorganic Matter*

Inorganic material appears usually in great excess. The ash content ranges between 33 and 90 %. It is rarely below 60 %, although there are known examples that some

Table 5.1 Tabular description of oil shale composition

The organic material	Bitumen (resolvent)	In a homogeneous mixture
	Kerogen (insoluble in organic and inorganic solvents)	
The inorganic material	Silicates, carbonates, pyrite and other mineral materials	

organic-rich sediments, such as Australian torbanite, exhibit only a small amount of ash (5 %). In the mineral part of various oil shales, clays (montmorillonite, illite, etc.), quartz, feldspar, carbonates (calcite, dolomite, siderite), pyrite, and rarely also nacholite ($NaHCO_3$), throne ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$), different phosphates, gypsum and some other minerals were identified (see Table 3.1). The moisture in oil shales is usually small.

5.3.2 Organic Matter

The organic matter of oil shales seems to account for smaller part of the sediment, only a few to several tens of percent (> 2 %), most typically 10–30 %. In some cases (for example in kukersite), organic matter content can reach more than 50 %. As noted above, most of the organic matter of oil shales is in the form of insoluble kerogen (up to over 95 %), and less is in the soluble form.

Optical examination of oil shale kerogens of different origin has shown that some of them are composed almost exclusively of algal material, while others represent a mixture of amorphous substance and recognizable organic remains. The main algal kerogen types are derived from freshwater-brackish algae, *Botryococcus*, which have been widespread from Precambrian to the present time, and from a variety of marine algae. In nature, it is difficult to find sediments with organic material that comes from only one species of organism.

Most of the organic material is usually in the form of amorphous kerogen, based on the H/C–O/C-ratio classified into several types, in the mixture with a small amount of defined organic residues. Amorphous material, which is often called sapropelic, is the result of microbiological transformation of biomass during the formation of sediment. In a homogeneous mixture with the mineral material it makes the world's richest accumulations of oil shales in the USA and Brazil.

The organic part of the shales may derive from planktonic organisms, and the microorganisms that inhabit sediments that have just been deposited. The composition of oil shale organic matter depends on the type of kerogen. Therefore, it ranges within wide limits. Carbon content is within the limits of 60–90 %, and hydrogen is usually high, so that the H/C ratio range from 1.25 to 1.75. Oxygen content is different, and O/C ratios are within the limits of 0.02–0.20.

Oil shale kerogens are most often type I and II. Contents of type III kerogen originating from higher plants, is lower. Type I kerogens are characterised with high contents of long aliphatic chains, and type II kerogens also with the contents of alicyclic and partly aromatic material. Differences in the composition and structure of oil shale kerogen are mainly due to differences in the precursor material, but also of various degrees of degradation of organic residues during the deposition of sediment.

Inorganic and organic materials of oil shales are sometimes intimately mixed so that it can be distinguished hardly under a microscope. Furthermore, they cannot be effectively separated from each other from homogeneous mixtures by physical methods. Since they are relatively accessible, and regarding the huge reserves, oil shales were and still are of great interest as a substrate for various organic-geochemical, chemical, technological and other types of research.

5.4 Use of Oil Shales

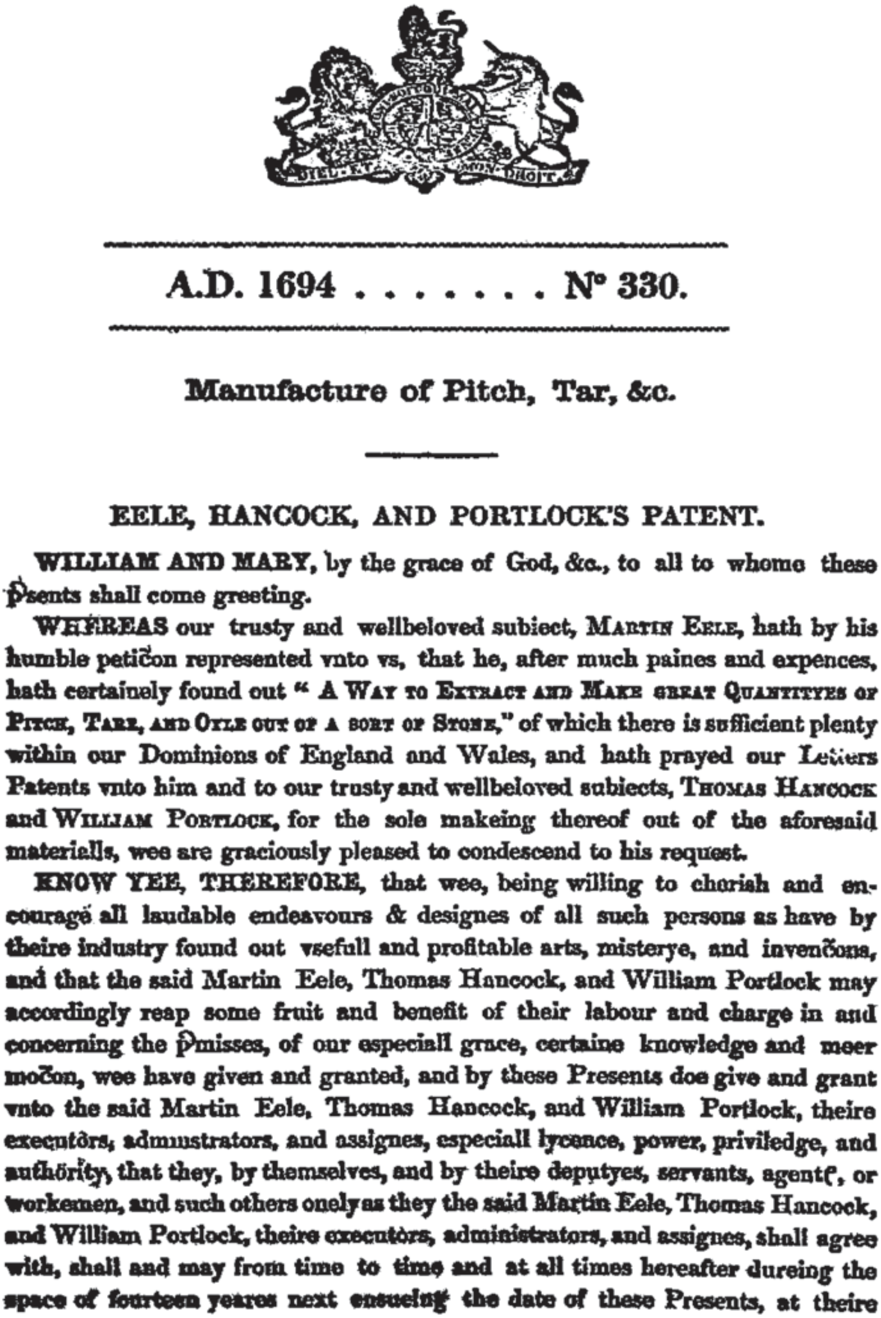
The history of shale processing is very old. The first mention of the possibility "of obtaining large amounts of resin, tar and oil from one type of stone" is found in the British patent no. 330 of 1694 (Fig. 5.2).When the oil shale is heated without access of air to about 500 °C (pyrolysis), organic material (mainly kerogen) decomposes to oil, some gaseous products, and solid residue, rich in carbon, which is left with the mineral material in the form of semicoke.

Production in almost all industrial plants (although with relatively small capacities) in which oil was produced from oil shales was suspended, primarily because the pyrolytic processing is expensive and creates serious environmental problems, so that fuels derived from shales could not compete with fuels from oil. Therefore, oil shales today are still only a potential alternative source of energy, and the study of technological procedures for their processing have been intensified or suspended depending on the seriousness of the world's "energy crises" and movement of oil prices in the world market.

Based on the previously reported data on the quantitative importance of kerogen in the Earth's crust (Fig. 2.16), it can be estimated that about 10^{17} kg of kerogen exist in the form of richer oil shales. From this quantity about 5×10^{14} kg of crude oil, so called "synthetic oil" can be obtained theoretically by pyrolysis. As it is evidently a huge energy potential oil shale is still attracting attention as a prospective source of energy and raw materials.

Pyrolysis is the basic and the most important possibility of its economic exploitation. Pyrolysis of oil shales can be compared with catagenetic processes of kerogen at the appropriate depths in the Earth's crust. Pyrolytic decomposition of oil shale kerogen in retorts is much faster due to much higher temperature compared with the temperature in the sediments in catagenetic zone, and therefore, the kinetics of pyrolysis reactions in the industrial furnaces is very different from the kinetics of reactions that occur in source rocks in geological time at much lower temperatures. The processes that occur during heating of shale kerogen in industrial furnaces are similar to processes during the laboratory simulation of geological changes of kerogen, e.g. during thermogravimetric analysis of sediment or testing by similar laboratory methods. As a result of the mentioned differences, crude oil obtained from oil shales differs significantly by composition from bitumen from source rocks and natural oil.

Finally, it should be noted that the oil shales and source rocks for oil differ in organic matter content. As it will be seen later, sediments, even with only about 0.5 % organic carbon can be conditionally considered as source rocks for oil and oil shale should contain a significantly greater amount of organic matter to be of interest for the pyrolytic processing, i.e. must contain more than the amount which would serve



A.D. 1694 . . . . Nº 330.

Manufacture of Pitch, Tar, &c.

EELE, HANCOCK, AND PORTLOCK'S PATENT.

WILLIAM AND MARY, by the grace of God, &c., to all to whome these ꝑsents shall come greeting.

WHEREAS our trusty and wellbeloved subiect, MARTIN EELE, hath by his humble petic̃on represented vnto vs, that he, after much paines and expences, hath certainely found out "A WAY TO EXTRACT AND MAKE GREAT QUANTITYES OF PITCH, TARR, AND OYLE OUT OF A SORT OF STONE," of which there is sufficient plenty within our Dominions of England and Wales, and hath prayed our Letters Patents vnto him and to our trusty and wellbeloved subiects, THOMAS HANCOCK and WILLIAM PORTLOCK, for the sole makeing thereof out of the aforesaid materialls, wee are graciously pleased to condescend to his request.

KNOW YEE, THEREFORE, that wee, being willing to cherish and encourage all laudable endeavours & designes of all such persons as have by theire industry found out vsefull and profitable arts, misterye, and invenc̃ons, and that the said Martin Eele, Thomas Hancock, and William Portlock may accordingly reap some fruit and benefit of their labour and charge in and concerning the ꝑmisses, of our especiall grace, certaine knowledge and meer moc̃on, wee have given and granted, and by these Presents doe give and grant vnto the said Martin Eele, Thomas Hancock, and William Portlock, theire executors, administrators, and assignes, especiall lycence, power, priviledge, and authority, that they, by themselves, and by theire deputyes, servants, agentꝭ, or workemen, and such others onely as they the said Martin Eele, Thomas Hancock, and William Portlock, theire executors, administrators, and assignes, shall agree with, shall and may from time to time and at all times hereafter dureing the space of fourteen yeares next ensueing the date of these Presents, at theire

Fig. 5.2 First page of the patent from the year 1694 as an energy source of the pyrolysis itself. Difference appear also in the organic matter maturity. As already mentioned, oil shale kerogen, regardless of the age of sediments, is immature, or is in the phase of early catagenesis (about 0.70 % Rr).

Box 5.2: Excursus

The most significant deposits and examples of shale processing industry

Oil shales are more widespread than it is generally realised, but the larger and richer deposits of great potential are found only in a relatively small number of countries: USA, Brazil, UK (Scotland), Russia, Estonia, France, Spain, South Africa, Australia, China and Serbia. As an illustration of their richness it can be stated that in only one, by the way very well-known deposit in the USA, Green River formation in Colorado, the estimated reserves of organic matter are approximate to the total world oil reserves.

At the first half of the nineteenth century, so before the first large oil deposits were found by drilling in Pennsylvania, shale processing industry was recorded in France (Autun 1838–1957 and St. Hilaire 1943–1948), Scotland (1848–1963), Kashpir (Russia, 1860–?), Canada (1860), Germany (Messel 1884–1963, Württemberg 1938–1949), Australia (1865, 1947–1952), Brazil (1881, 1897–?), New Zealand (1900–1911), Switzerland (1915), Soviet Union (Estonia 1921–, Slance 1952–), Sweden (1921, 1941–1960), Spain (1922–1966), China (1929–), South Africa (1935–1962), USA (a pilot plant in 1944) and Israel (a pilot plant in 1952).

Considering their potential importance, the main approaches to thermal processing of bituminous shales should be understood. The classical way of processing is the aboveground dry distillation. The shale rock is first mined, crushed, and then heated to a certain temperature in the absence of air (pyrolysis). For this type of processing, a number of different types of special furnaces—retorts (the term "retorting", used for shale processing, has been derived from it) were used or tested. Retorts differ very much from each other in structure, mode of heat transfer and other technical details. Possibilities for heating the shale in retorts are also different: outside, through walls, or directly in the retort, by combustion of a part of shale or with a gaseous or even solid heat carrier. Aboveground processing is expensive, because the entire mass of rock is moved from the deposit, then it is all heated, absorbing a large amount of heat, to obtain only a relatively small amount of crude oil. Most of the shale is remains as a solid semicoke residue, from which the major problems originate, especially from the viewpoint of environmental protection. Namely, the semicoke is easily powdered and spread by wind, and contains sulphides that, when exposed to atmospheric influences, break down polluting the air. On the other hand, washing admixtures contaminates waters. Above all, in order to make savings in transportation, shale must be processed on site, often under conditions that are not much favorable, e.g. in areas where water is scarce and far from consumption centres.

Another option of processing is the underground pyrolysis. In this case, the sediment is not mined, but it is processed in the deposit ("*in situ*"). More than a few decades ago, extensive research of underground distillation was conducted, aimed at addressing the problems encountered with conventional aboveground processing of oil shale, such as environmental protection, high mining costs, disposal of semicoke. The essence of this type of processing is as follows: shale remains in the deposit, there it is crushed (by controlled explosions), and then in so built-up underground "retorts" of large dimensions it is heated by some suitable heat carrier. Oil is collected in collection channels and reservoirs and pumped from there. The biggest problems with these procedures are in the preparation of underground retort, control of the movement of "fire front" and in the relatively small yields of oil, i.e. low overall exploitation of shale organic matter. Technological procedures for thermal processing of oil shales are being tested also nowadays.

The yield of crude oil depends on the richness of raw material (organic matter content), type of kerogen and mineral composition, and also the technology applied. Calculated on the total amount of organic matter, it could be expected with the use of pyrolysis getting the yields of crude oil from 20 % to a maximum of about 65 %.

In a laboratory, the potential of oil shale is estimated by common standardised technical analysis, pyrolysis in the aluminium retort by Fischer. Schematic display is shown in Fig. 5.3. Measured quantity of crushed shale (normally 50 g) is heated

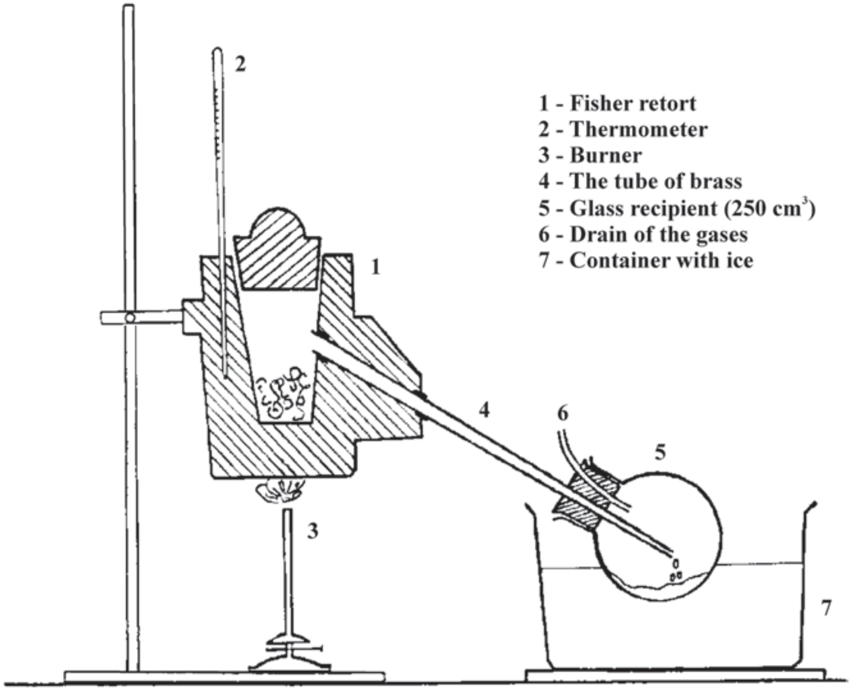


Fig. 5.3 A standard Fischer apparatus for oil shale investigation

in a retort programmed with speed within half an hour to 520 °C, and heating at this temperature is continued for another 15 min. Liquid products (crude oil and water) are caught in a bubble immersed in an ice bath. For corrections, the water content is determined according to Dean-Stark.

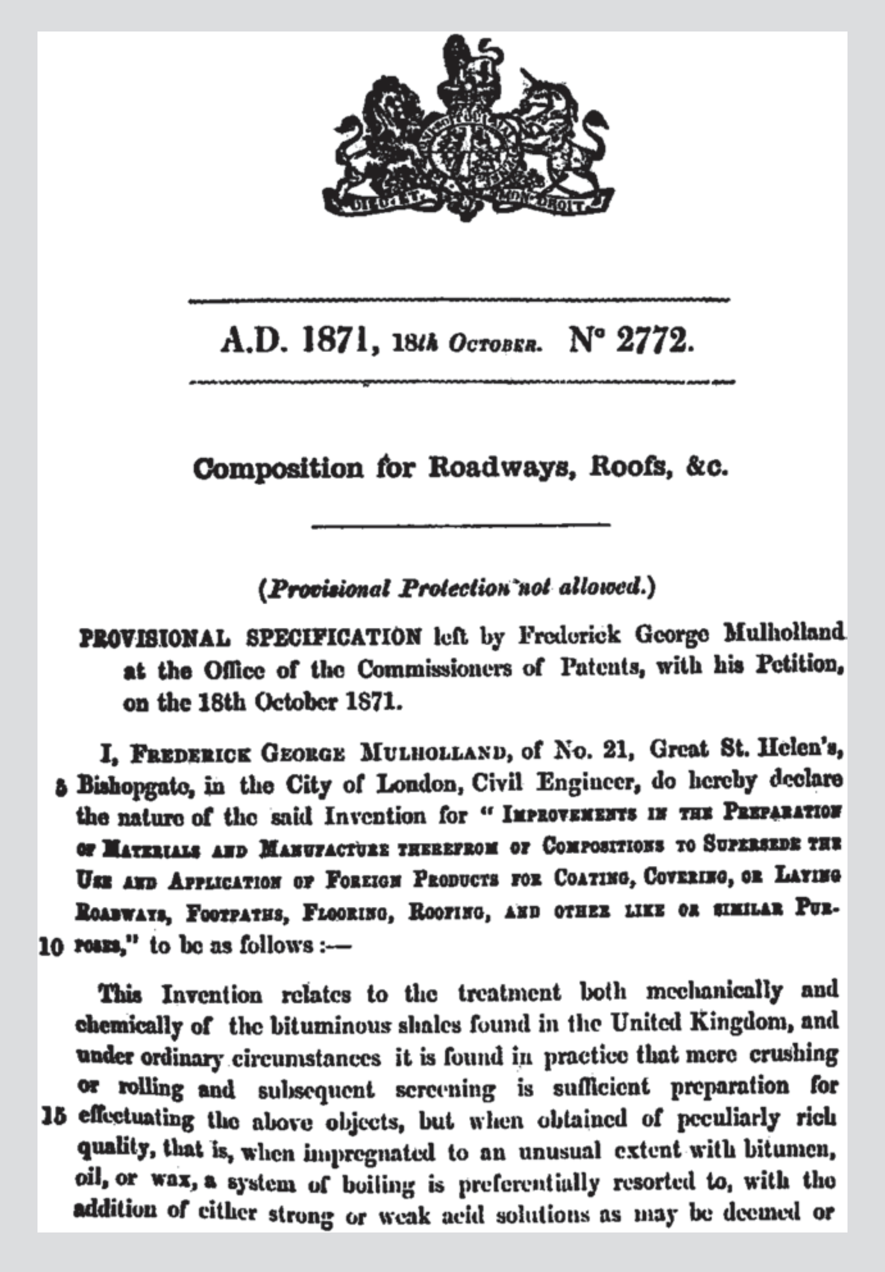
The lower yield limit for the economical processing of oil shales is about 2.5 % of oil. However, in practice it was proven that it is necessary for the limit yield to be at least about 5 %.

The crude oil may contain up to 2 % nitrogen, up to 8 % sulphur and 30–50 % of unsaturated compounds. This crude material is processed to produce gasoline, diesel oil, heating oil, lubricating oil, bitumen (asphalt residue), petroleum coke, various resins and waxes (paraffin) and other less important products. As it has already been mentioned, in addition to oil, gas and semicoke are also obtained by pyrolysis.

Box 5.3: Excursus

Oil shales can have multiple use

Given the specific composition and properties of oil shale, many other possibilities for its utilisation were studied, either as energy source or as raw material. The possibility of processing by gasification, use in cement and brick industry as a supplemental fuel and raw material, use as filler in asphalt mixes, application in the production of electricity by direct combustion, applications as petrochemical feedstock (e.g. to obtain organic acids by kerogen oxidation), obtaining rare elements from the ashes, obtaining substances with antibiotic action, obtaining low-cost adsorbents etc. The example of patenting mixtures for roads and roofs with oil shale as a component, back in 1871, is shown below.



A.D. 1871, 18th October. N° 2772.

Composition for Roadways, Roofs, &c.

(Provisional Protection not allowed.)

PROVISIONAL SPECIFICATION left by Frederick George Mulholland at the Office of the Commissioners of Patents, with his Petition, on the 18th October 1871.

I, FREDERICK GEORGE MULHOLLAND, of No. 21, Great St. Helen's, Bishopgate, in the City of London, Civil Engineer, do hereby declare the nature of the said Invention for "IMPROVEMENTS IN THE PREPARATION OF MATERIALS AND MANUFACTURE THEREFROM OF COMPOSITIONS TO SUPERSEDE THE USE AND APPLICATION OF FOREIGN PRODUCTS FOR COATING, COVERING, OR LAYING ROADWAYS, FOOTPATHS, FLOORING, ROOFING, AND OTHER LIKE OR SIMILAR PURPOSES," to be as follows:—

This Invention relates to the treatment both mechanically and chemically of the bituminous shales found in the United Kingdom, and under ordinary circumstances it is found in practice that mere crushing or rolling and subsequent screening is sufficient preparation for effectuating the above objects, but when obtained of peculiarly rich quality, that is, when impregnated to an unusual extent with bitumen, oil, or wax, a system of boiling is preferentially resorted to, with the addition of either strong or weak acid solutions as may be deemed or