Journal of Thermal Analysis and Calorimetry, Vol. 71 (2003) 905–914

DIVERSIFICATION OF NATURAL RESINS OF VARIOUS ORIGIN

Oxyreactive thermal analysis and infrared spectroscopy

S. Cebulak[1], *A. Matuszewska*[1] *and A. Langier-Kuźniarowa*[2]*

[1]Silesian University, Dept. of Earth Sciences, 41-200 Sosnowiec, 60 Będzińska str., Poland
[2]Polish Geological Institute, 00-975 Warszawa, 4 Rakowiecka str., Poland

Abstract

The paper presents the applicability of oxyreactive thermal analysis (OTA) for the investigation of different kinds of resins both natural (recent and fossil) and synthetic. For comparative reasons and a more precise interpretation, along with OTA infrared spectroscopy was used as a method commonly applied for the investigation of fossil resins. The results obtained prove that the OTA method may be very useful for diversification of different kinds of resins. The parameter most valuable for the preliminary characteristics of resins and the evaluation of their transformation was found to be the mass loss recorded on TG curves in three definite temperature ranges.

Keywords: amber, organic matter maturation, oxyreactive thermal analysis, resins

Introduction

Interesting results were obtained from many years' research work on the use of oxyreactive thermal analysis (OTA) for investigations of various organic matter types of natural origin [1–4]. These results encouraged the present authors to test the possible application of the OTA method for analysis of organic matter of natural resins (recent and fossil) as well as, for comparative reasons, of synthetic resins.

To confirm the applicability of the OTA method for this purpose the authors investigated resins using parallel the OTA and infrared spectroscopy (IR) methods. The IR method, broadly employed for investigations of fossil resins, is here a comparative method also enabling a more extensive interpretation of the OTA results. These two techniques are now frequently used for comparative reasons [5–8].

The application of the OTA method for studies of fossil resins presented in this paper was preceded by the research of Savkevich [9] who suggested that the diversification of the shapes of the TA diagrams can serve as diagnostic for fossil resins of various origin.

---

* Author for correspondence: E-mail: tzych@pgi.waw.pl

1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Also in this study an attempt has been made to use these diagnostic possibilities indicating considerable potential possibilities of oxyreactive thermal analytical techniques.

Experimental

The oxyreactive thermal analysis (OTA) was used as the tool for thermal investigations. The OTA procedure applied was particularly suitable for examination of the organic matter. The samples (mass of 80–20 mg of organic matter) ultrafinely ground to the particle size of 0.2–0.3 μm, diluted with Al_2O_3 (analyte to alumina 1:3) were placed on a multiplate sample holder with 2 or 4 plates in a dynamic air atmosphere. The Hungarian derivatograph a simultaneous TG/DTG/DTA instrument developed by Paulik, Paulik and Erdey was used.

The absorption spectra in the infrared range (IR) were obtained by a technique of potassium bromide pellets (analyte to KBr 1:230) using the Magna System 560 FT IR apparatus manufactured by Nicolet.

Discussion of results

OTA method

In the presented work the OTA method was used for investigation of organic matter following the principles of this method. The results obtained enabled to calculate the percentage of mass loss for the analyzed samples resulted from characteristically diversified reactions in the oxidation conditions. This diversification is an effect of different susceptibility of samples to the mentioned process in specified temperature ranges. The observed differences of the thermal curves course are a function of different composition, structure and reactivity of samples under investigations.

The analysis of the thermal curves course enabled to define three following temperature ranges characterizing three main stages in the oxidation conditions:

I: temperatures up to 260–270°C – in this range the fractions of low-temperature volatile matter are mainly released; in the case of some samples the oxidation processes proceed to an insignificant degree also in this range;

II: temperature range from 260/270 to 390/400°C – the main stage under oxidizing conditions; very reactive fragments of the structure of analyzed samples undergo this process;

III: temperatures above 390–400°C – under oxidizing conditions correspond to the processes of lower enthalpy and dynamics than in the II temperature range.

In spite of the preliminary character of the described investigations the results obtained by OTA and IR (for comparison) clearly show the applicability of the OTA method for diversification of composition and structure of analyzed sample types. This is illustrated by a triangular diagram (Fig. 1) where each sample is illustrated by a point. The coordinates (I, II, III) of the points are the percentages of the loss of mass estimated from thermogravimetric curves in three temperature ranges described above.

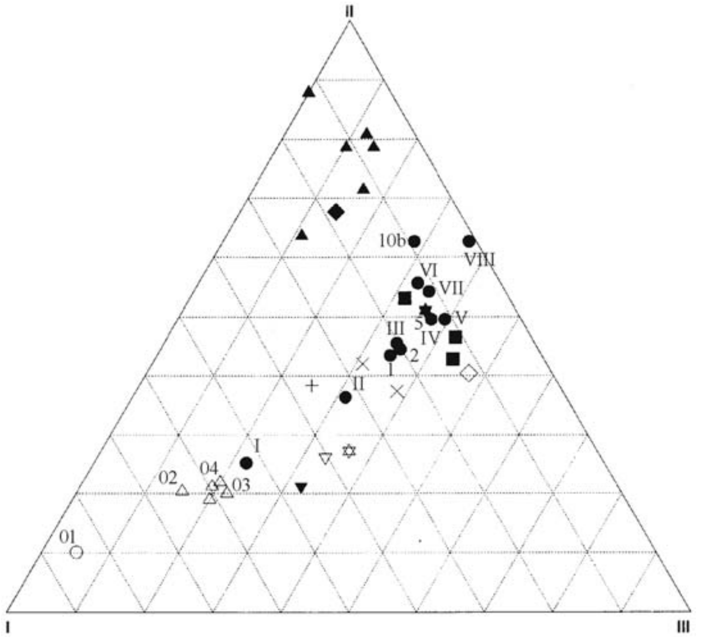

Fig. 1 Classification diagram of fossil resins and similar matter according to the OTA results. I – reactive fraction in temp. to 260–270°C; II – reactive fraction in temp. 260–270 to 390–400°C; III – reactive fraction in temp. above 390–400°C. ● – Succinites: (I) B-2, (II) covering layer, (III) Bitterfeld, (IV) No-5, (V) Baltic (standard), (VI) bone type, (VII) white, (VIII) brandy brown and No-1, No-2, No-5, No10 b, spotted, white porous, Baltic after extraction; ■ – Cretaceous fossil resins: Galicia-Spain, New Jersey, Jordan - other fossil resins: ✶ – Dominicana, ✡ – Glessite, ▼ – Krantzite, ▽ – Borneo, ◆ – Siegburgite, ◇ – Coral (Corallium negrum), × – Copales: Madagascar, Columbia, + – Kauri, ▲ – Imitation of ambers: Africans No 1, No 2, No 3 and plastics: polyester, polystyrene, poly(methyl)metacrylate, △ – precursors for fossil resins: (02) Colophony recent and subfossil, (03) pine resin, young fossil resin, (04) mirrh, o – Succinic acid (01), (I, II...VIII, 01...04) from this sample the TA curves are presented on Figs 1 and 2

The majority of the points form a band which could be called ‘maturation band’ of organic matter of fossil resins. The points of siegburgite samples and synthetic polymers are located outside this band. Siegburgite is the fossil resin originating from Bitterfeld region (Germany) [10]. This resin of natural polystyrene character [11,12] was formed probably by polymerization of cinnamic acid identified in a molecular phase of this fossil resin [13]. The similarity of the DTA and DTG curve shapes of siegburgite and synthetic polystyrene is presented in Fig. 2.

In the analyzed group of natural resins a maximal content of low-volatile products (I range of temperatures) is characteristic of the sample group 02–04: pine resin, myrrh, colophony samples and so-called ‘young amber’, according to description given by the amber collectors. A high contribution of low-volatile fraction in the case

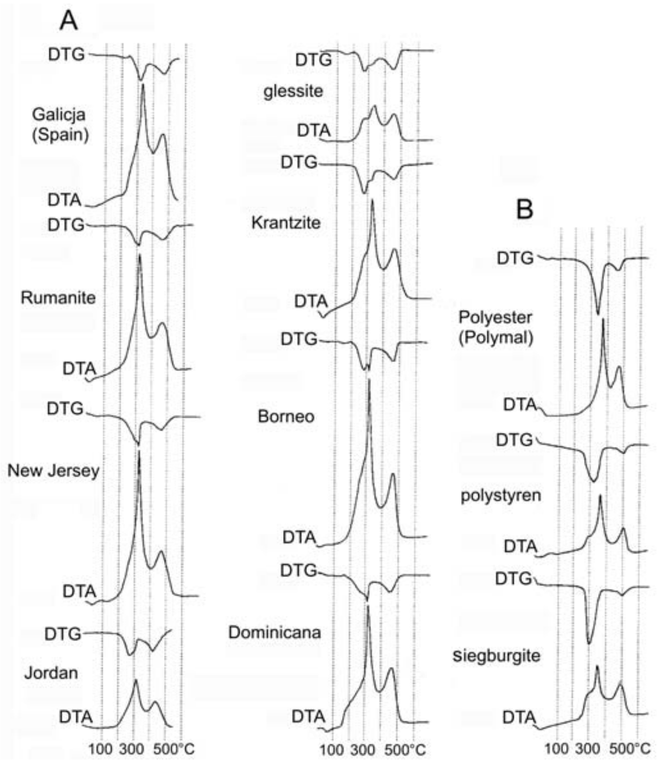

Fig. 2 DTA and DTG curves of: A – fossil resins of various geological age, B – siegburgite and chosen polymers

of this group of samples is illustrated distinctly by DTA and DTG curve shapes (Fig. 3) as well as by positions of respective points on the triangular diagram (Fig. 1).

The succinic acid sample (01) has taken an expected, more terminal else, position on the triangular diagram. This compound is one of the components of the molecular phase of succinite type fossil resins. The points deriving from succinite samples are placed on the diagram in the second terminal part of the ‘maturation band’ (samples II-VIII).The succinites are Tertiary resins of a considerable degree of diagenesis which signifies a relatively high degree of transformation of their chemical structure, probably also in the direction of a higher cross-linking of the resin macromolecules.

The resins called ‘copals’ and kauri gum show a lower cross-linking of the structure in comparison with succinite samples of advanced degree of diagenesis. There is a considerable difference in the geological age of these two groups of samples. The succinites are Tertiary (about 40 millions years old) while the copals are resins of age defined as not more than several millions years [14]. The analyzed kauri gum is of unknown age. However, the position of the point of this resin on the diagram (among points attributed to the copals) enabled to include this sample to the copals group.

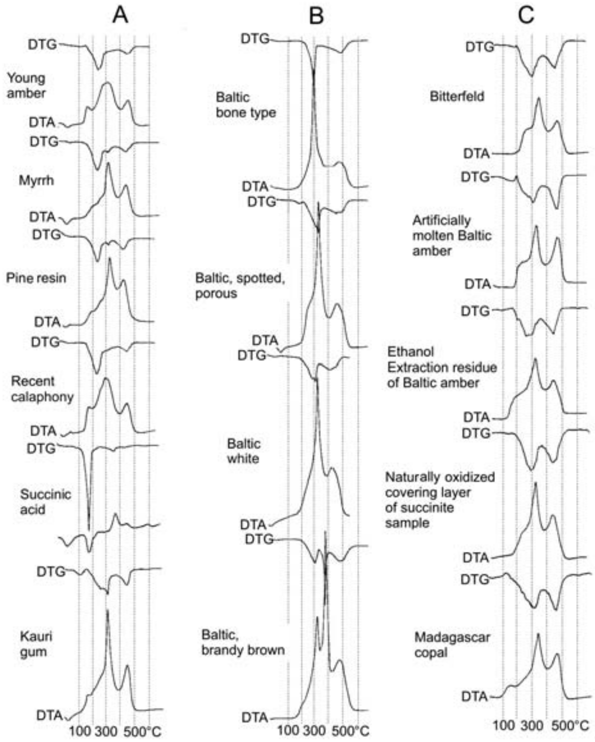

Fig. 3 DTA and DTG curves of: A – some recent and young fossil resins, colophony samples, succinic acid and Kauri gum, B – and C – various types of succinite samples and Madagascar copal

On the triangular diagram, in the proximity of the points corresponding to succinite samples, occur points representing older resins – from Cretaceous times. It may suggest small changes of macromolecular structure of fossil resin in this range of diagenesis (Tertiary–Cretaceous). For this comparison, however, the similarity of main structural features of the parent plant resins of these two types of fossil resins should be assumed.

The ‘maturation band’ obtained with the use of the OTA method indicates therefore the general tendency of the reactivity changes (being a result of the structure transformations in the range: from recent resins up to analyzed Tertiary and Cretaceous ones). Some exceptions are, however, noticed here. Three points corresponding to Tertiary resins (from Borneo, as well as glessite and krantzite from Bitterfeld, Germany) are placed on the triangular diagram below the main ‘maturation band’, further down than the points attributed to copal samples. The respective thermal curves of samples under discussion (Fig. 2) confirm also considerable mass losses in lower temperature ranges. The genetic difference in relation to other analyzed samples may be a reason of this wide dissimilarity in the case of glessite and resin from Borneo. The krantzite resin differs from all other investigated samples by a higher sulfur content.

A comparison of thermal curves of the particular resins of the succinite type (Figs 3B and C) seems also to be interesting. Distinctive are samples transformed to a certain degree by natural or laboratory processes. A considerable similarity was observed for example for the molten succinite and succinite from Bitterfeld (Fig. 3C). The shapes of DTA and DTG curves show also distinctly individual character of samples: 'brandy brown', 'Baltic, spotted', 'white' and 'bone' type (Fig. 3B). The differences can result from different geological and geochemical history of samples under discussion.

The results obtained indicate that the OTA method may also be of a great importance for diagnosis and comparison of Tertiary and Cretaceous resins from various deposits.

It was e.g. stated that a general course of the thermal cures is similar for Tertiary resins from Dominicana and from the Baltic Sea (Figs 2A and 3B), despite various tree species attributed to the resins: deciduous trees and conifers, respectively [15]. This observation may be a contribution to further discussions on the genesis of fossil resins.

Also interesting is the conformity of thermal curves of Cretaceous resins (from Spain and USA) (Fig. 2A) in spite of considerable distances between the deposition sites. The position of respective points on the diagram (Fig. 1) is also similar. These points are, moreover, placed near the point of the Corallium negrum analyzed here for comparison. Chemical composition of this coral seems to have the features of chitinoid structure [16].

Figure 2A shows a thermal curve of rumanite from Sakhaline (Russia). It is a Tertiary resin but the course of the thermal curve is similar to these of the above mentioned Cretaceous resins. It was stated, however, that rumanite is probably a succinite transformed under natural conditions with elevated temperature and pressure [17].

The Cretaceous resin from Jordan differs somewhat in properties from other Cretaceous resins analyzed here. The shapes of DTA and DTG curves are similar to these of naturally oxidized covering layer of succinite sample (Fig. 3C). For the resin from Jordan, however, a lower amount of volatile products was observed in the lowest temperature range (I).

Infrared spectroscopy (IR)

Infrared spectroscopy was used for preliminary characteristics of the analyzed samples. This method was applied also for supporting interpretation of the results obtained by the OTA method. IR spectroscopy is very helpful for the analysis of fossil resins because of specific infrared spectra shapes, being the 'fingerprints' of various types of resins. It can be useful for comparisons and identification. Owing to the characteristics of chemical structure of resins the infrared spectra enable a preliminary classification of the resins on the basis of similarity of the spectra shapes or by differences in the degree of diagenetic transformations of the structure. The IR spectra, illustrating differences in the chemical structure also contribute to the discussion of the differences between reactivity of resins.

Infrared spectroscopy is a particularly efficient method in unfailing identification of succinite type of fossil resins because of a characteristic absorption band in the range of about 1150–1260 cm^{-1} (Fig. 4). This is the so-called 'Baltic shoulder'. This name derives from another designation of succinite: 'Baltic amber' and from abundant occurrence of succinite in the Baltic region. 'Baltic shoulder' originates probably from ester groups in the chemical structure of succinite. Figure 4 shows the IR spectra of several succinite samples derived from various deposits, i.e. from Sambia Peninsula (Russia) (Fig. 4a) or from Bitterfeld (Germany) (Fig. 4b). The general shape of the spectrum was not changed as the results of the ethanol extraction (Fig. 4c). This signifies that there is an unextractable, macromolecular phase of structure which influences mainly the shape of the IR spectra of succinite. Infrared spectrum did not reveal any distinct changes in a spectrum of naturally oxidized succinite (weathered covering layer) (Fig. 4d). In this case the changes of the structure were shown better by the OTA results as illustrated e.g. by the position of respective point on the triangular diagram (among points of copals) (Fig. 1). It is probably an effect of the oxidation process. This process can be the reason for a partial destruction of macromolecular structure. An increase of loss of mass in the lowest I range of temperatures (Fig. 1) seems to confirm this hypothesis.

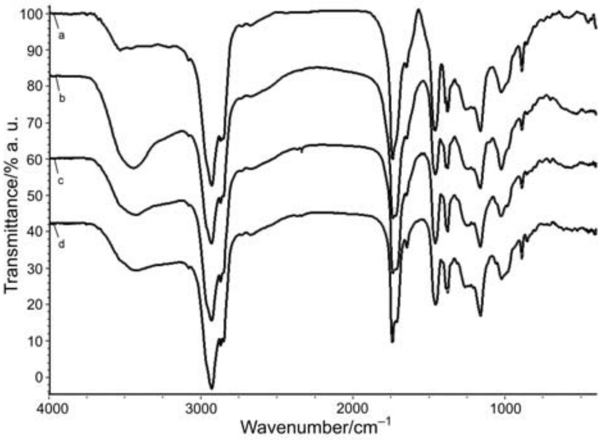

Fig. 4 Infrared spectra of succinite type samples with characteristic band called 'Baltic shoulder' in the range of wavelength of 1150–1260 cm^{-1}: a – amber from Sambia Peninsula (Russia), b – amber from Bitterfeld (Germany), c – ethanol extraction residue of Baltic amber, d – naturally oxidized covering layer of succinite sample

Also of great value for the diagnostics of resins on the basis of the IR spectra is the relative intensity of band of oxygen groups at about 1700 cm^{-1}. A direct relationship is observed. This is in accordance with the tendencies indicated also for other types of fossil organic matter [16].

For the analyzed series of recent resins the intensity of the band mentioned is strongly dominating in their IR spectra (Fig. 5). The relative intensities of the bands at about 1700 cm^{-1} are lower in the IR spectra of a series of older – e.g. succinite type resins (Fig. 4). This tendency progresses in the direction of Cretaceous resins. However, some exceptions were observed for two Tertiary resins, from Borneo and

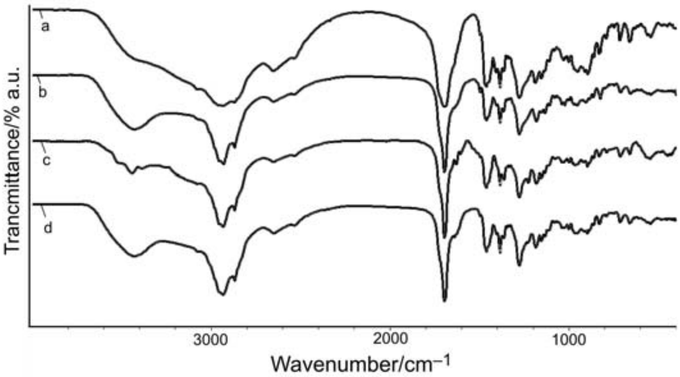

Fig. 5 Infrared spectra of recent resins: a – myrrh, b – pine resin, c – recent colophony, d – subfossil colophony

glessite, which do not comply with the above regularity. The distinct dissimilarity of these samples was also confirmed by the results of analysis by the OTA method.

A band of unsaturated bonds of the exocyclic diene type in terpenoids (at about 890 cm^{-1}) [18] is an other diagnostic band here. The relative intensity of this band is the greatest in the IR spectra of copals. The bands of this type (but of lower intensity) are also observed in the IR spectra of succinites as well as in the spectrum of the resin from Dominicana. (The point of the latter is near to the points of succinite samples on the triangular diagram described earlier (Fig. 1).)

Most probably the reactive unsaturated groups are an important source of volatile products in the ranges of lower temperature (I and II) which results in the position of respective points on the triangular diagram.

The case of rumanite resin is an other example of confirmation by IR analysis of the results obtained by the OTA method. The similarity of thermal characteristics of this Tertiary resin and the analyzed Cretaceous ones have been described earlier. Infrared spectra of rumanite and the analysed Cretaceous samples show as well a significant similarity. The IR spectrum of rumanite has, however, some features which can confirm the statement [19] that this resin is probably a product of treatment of succinite by elevated pressure and temperature under natural conditions.

The similarity of the IR spectra of siegburgite and synthetic polystyrene [12] confirms the approximate position of respective points on the triangular diagram (Fig. 1). In the same area of the diagram the other synthetic polymers have also respective points. This position on the diagram indicates a low amount of volatile products (I temperature range) and a dominating contribution of structures reactive in II temperature range. It may be an effect of a regular structure and lower degree of cross-linking of synthetic polymer structures, as compared e. g., with fossil resins of high degree of diagenesis.

Conclusions

The results obtained indicate that the method of the oxyreactive thermal analysis can be useful for preliminary characteristics of resins and for estimation of diversification of the structure by comparison of their reactivity in the specified experimental conditions. The OTA method may be also applied for description of the diagenetic transformation degree of chemical structure of fossil resins.

A numerical parameter proved promising for classification purposes estimated from TQ. This parameter is calculated from a set (characteristic for each analysed sample) of mass loss of percentages for three ranges of temperatures fixed for the given experiment.

The usefulness of the applied technique of measurements and helpfulness of used numerical parameter are illustrated in this work on the triangular diagram. The points characterizing particular samples of natural resins form a band which may be called the ‘maturation band’ of fossil resins. This band begins with the point of the succinic acid of simple molecule and is followed by points of recent resins and finally by points of copals. All those samples can be characterized by a relative high yield of low-volatile products of proceeding processes. The samples of fossil resins represented by points marked on further part of ‘maturation band’ are characterized, in turn, by lower yield of low-temperature volatile products. These last mentioned samples are Tertiary and Cretaceous resins of probably higher degree of cross-linking of their structure in comparison with younger resins.

The resins represented by points outside the main ‘maturation band’ confirm also the usefulness of the applied method revealing the specific features of resins of various origin.

The results of investigations, made for comparison, of synthetic polymers suggest that macromolecular construction of natural resins is not so regular. Moreover, cross-linking of the structure’s natural resins of higher degree of diagenesis is probably higher than this of synthetic polymers.

The results obtained indicate the possibilities of application of the OTA method as one of methods helpful for classification of resins both recent and fossil of various degree of diagenesis. For further investigations the population of analyzed samples, however, should be more numerous and more diversified. A simultaneous application of IR method and OTA to verify the results is also advisable.

References

1 S. Cebulak and M. Pliński, Oceanology, 38 (1996) 99.
2 J. Pacha and S. Cebulak, IMSS, (1997) 463.
3 S. Cebulak and A. Langier-Kuźniarowa, J. Thermal Anal., 48 (1997) 163.
4 S. Cebulak and A. Langier-Kuźniarowa, J. Thermal Anal., 50 (1997) 175.
5 S. Alam, L. D. Kandpal and G. N. Mathur, J. Thermal Anal. Cal. 64 (2001) 487.
6 I. M. M. Kenawy, M. A. H. Hafez and R. R. Lashein, J. Therm. Anal. Cal. 65 (2001) 723.
7 M. A. Villetti, J. S. Crespo, M. S. Soldi, A. T. N. Pires, R. Borsali and V. Soldi, J. Thermal Anal. Cal. 67 (2002) 295.

8 J. Ledru, B. Youssef, J. M. Saiterjean and J. Grenet, J. Thermal Anal. Cal. 68 (2002) 767.

9 S. S. Savkevich and I. A. Shaks, Žurnal Prikladnoj Chimii, a/ 37 (1964) 930.; b/ 37 (1964) 1120.

10 G. Krumbiegel and B. Krumbiegel, Fossilien, S 7 (1996) 112.

11 B. Kosmowska-Ceranowicz, Est. Mus. Cienc. Nat. de Alava, 14 (1999) 73.

12 A. Matuszewska, R. Wrzalik and A. Hacura, Prace Muzeum Ziemi PAN, 46 (2001) 67.

13 H. Klinger and R. Pitschki, Berichte Dt. Chem. Ges., 17 (1884) 2742.

14 O. Faber, L. B. Frandsen and M. Plough, Amber, Ravmuset, Varde, Denmark 2000, p. 6.

15 G. O. Poinar Jr., Life in Amber, Stanford, California 1992.

16 A. Matuszewska, R. Wrzalik and J. Ożdżeński, Polski Jubiler, 14 (2001) 50.

17 E. C. Stout, C. W. Beck and K. B. Anderson, Phys. Chem. Minerals, 27 (2000) 665.

18 S. Jasieńko, A. Matuszewska and A. John, Fuel Process. Technol., 41 (1995) 207.

19 E. C. Stout, C. Beck and B. Kosmowska-Ceranowicz, in: K. B. Anderson, J. C. Crelling (Eds), Amber, Resinite and Fossil Resins, ACS Symp. Ser., No. 617, Washington 1995, p. 130.