13 Birch bark tar

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A piece of wood tar was found at Schipluiden, displaying teeth imprints. Mass spectro-metry showed that the piece of wood tar is most probably birch tar to which some fats or plant oil and some beeswax were added. It is a unique find and a very early example of this mixture. The tar may have been used as chewing gum, as suggested by teeth imprints, and/or as an adhesive as testified by the presence of traces of tar on a quite a few flint implements.

13.1 Introduction (A.v.G.)

One of the most remarkable finds from Schipluiden is a piece of wood tar (no. 8005), which initially found its way into the lithic assemblage because no one recognised it for what it was (fig. 13.1). The piece is especially interesting because it shows imprints of teeth, indicating chewing. The piece is also broken. It would seem that this was (intentionally) done in the past, as the fracture was not fresh.

Wood tar is a natural resin that has been heated. Resins are non-cellular plant exudates that are insoluble in water and serve to protect plants and trees when they are damaged. Resin is produced by various tree species all over the world, for example pine. In northwestern Europe pine resin and birch bark tar have over the centuries been used by man for various purposes.

The earliest known evidence of the use of birch bark tar as an adhesive dates from the Mesolithic (Aveling/Heron 1999). Slow heating of strips of birch bark in the absence of oxygen leads to a process of distillation in which the volatile compounds of the resin are released and the remaining resin is allowed to cool and set. The resulting product is called wood tar or wood pitch. The method for producing birch bark tar commonly known from the Middle Ages involved the use of two pots placed on top of each other, with the top one having holes through which the tar could trickle into the bottom one (Kurzweil/Todtenhaupt 1991). Several experiments have been carried out over the years to reproduce the tar-making process in attempts to answer the question how this could have been realised without using a ceramic vessel as the retainer (*e.g.* Czarnowski/Neubauer 1990; Weiner 1988). The pitch can be mixed with for example beeswax to give it flexibility and make it less brittle. Chopped straw may be added for the same purpose: the fibres make the pitch less fragile. Wood ash is known to have been added to tar, too. The resulting wood tar survives well under anaerobic conditions.

In the past, resins and wood tar were used for a variety of purposes. In the first place, they were useful adhesives for hafting flint tools. Being insoluble in water, they were also used for waterproofing objects such as canoes and for sealing wells. A well at the *Bandkeramik* site of Erkelenz-Kückhoven yielded a piece of birch bark pitch that was probably used in the well's lining (Ruthenberg/Weiner 1997). Birch bark pitch was even used to decorate ceramic vessels (Vogt 1949). From ethnographic sources we know that pitch can also be used as a disinfectant and for soothing toothache. It is probably the earliest chewing gum (Pollard/Heron 1996). Being particularly inflammable, it may also have been used as some sort of candle (see the sticks of pitch found in North America reported in Gibby 1997). In the last fifteen years a considerable amount of archaeometric research has

Figure 13.1 Piece of birch bark tar (no. 8005) viewed from two sides (scale 1:1).

focused on the analysis of wood tar (*e.g*. Beck *et al*. 1997; Bonfield *et al*. 1997; Hayek *et al*. 1990; Heron *et al*. 1991; Regert/Rolando 2002; Regert 2004).

13.2 Fingerprinting the sample (J.B.)

13.2.1 Method

Direct Temperature resolved Mass Spectrometry (DTMS) was used as the analytical technique to fingerprint the sample. In principle, this method entails the mass spectrometric monitoring of a sample that is heated on a Pt/Rh filament. Compounds adsorbed onto or sequestered in the sample are evaporated, after which the non-volatile residue is thermally decomposed to smaller fragments. The result is a dataset that consists of mass spectra (mass range 20-1000 Dalton) recorded as a function of time/temperature. This method has been used for the analysis of complex organic materials, often in association with inorganic substances. Typical recent applications concerned carbonised grains and peas (Braadbaart 2004), carbonised food residues and coatings on ancient pottery (Oudemans/Boon 1996; Oudemans *et al*. 2005a, b). The method has recently been applied to various archaeological objects in the Louvre (Regent/Rolando 2002).

Aliquots of about 50 micrograms of powder were homogenised in ethanol in a glass micro-mortar and applied to the filament probe. The instrument used was a JEOL SX102-102A tandem mass spectrometer. The MS conditions were 16 eV electron ionisation, 8kV acceleration voltage, scan range m/z 20-1000 at a rate of 1 s/scan. Data were processed in a JMA7000 data system and software.

13.2.2 Results

The sample was analysed twice: once using a smaller relative amount (run 4007) and once using a more concentrated sample (run 4008). The TIC of 4007 (fig. 13.2a) shows a narrow high peak in the temperature range of cross-linked condensed materials (scan 65-90). The ion current in the scan range of scan 50-65 is evidence of sequestered non-chemically bonded compounds, that evaporate from the sample. The summation spectrum at 16 eV of the cross-linked material is shown in figure 13.2b. The DTMS spectrum shows some typical fragment ions deriving from pentacyclic triterpenoids (m/z 189, 203) and some (near) molecular ions at m/z 394, 396, 406, 424, 438. Some of these peaks are also observable in the spectrum of birch resins presented in the paper by Regert and Rolando (2002), but they used different analytical conditions: in their 70 eV spectrum the relative number of fragment ions was greater than in our 16eV spectrum. There is also a possibility of shifts in the molecular ions due to water loss or other eliminations due to electron ionisation. Further confirmation of the presence of pentacyclic triterpenoids can be seen in figure 13.2b, which shows evaporating compounds in the range of m/z 390-460. Assignment of the resin fraction to a birch resin is reasonable, but would require confirmation by further GCMS studies to identify the individual compounds.

The DTMS spectrum also shows peaks representing C16:0 and C18:0 fatty acids (m/z 256 and 284). They imply the addition of drying oil (unsaturated plant seed oil) or fats that could have been used to thicken the pitch. Evidence of traces of beeswax was observed. The beeswax peaks are at m/z 592, 620, 648, 676 and 704. The mass peaks at 634 and 662 are not usually observed in fresh beeswax, but they could represent oxidation products (the addition of oxygen resulting in an hydroxyl group would add 16 Dalton; peroxidation and stabilisation of the radical would lead to loss of hydrogen and the formation of a keto group, *i.e*. 14 Dalton higher mass). Note that the relative amount of beeswax is small (magnification factor 30×).

To conclude, the sample of find number 8005 consists mainly of a pentacyclic triterpenoid resin, possibly birch resin. The substance may have been modified with fats or plant oil and some beeswax.

13.3 Conclusion (A.v.G.)

The presence of birch bark tar among the finds could imply that hafting and retooling took place at the site (Keeley 1982). The use of birch bark tar as glue is attested from the Mesolithic, possibly even earlier. Some of the stone tools found at Schipluiden show evidence of hafting (see chapter 7, fig. 13.3). In some cases small black specks were observed at points that may be assumed to represent the most obvious places for a haft (*i.e*. opposite a scraper edge or on the distal part of an arrowhead). Such evidence was observed especially on the arrowheads. Thirteen arrowheads show evidence of hafting and on nine of them black tar remains were observed (section 7.7.10). This makes it very likely that tar was used as an adhesive for fixing stone tools to their wooden, bone or antler hafts. Among the wooden artefacts found at Schipluiden are eight parts of axe handles and two possible adze hafts (chapter 11). The bone and antler assemblage however contains no hafts (chapter 10), contrary to for example that of the late Mesolithic sites of Hardinxveld-Giessendam (Louwe Kooijmans *et al*. 2001a, b). The number of hafts found at Schipluiden may therefore seem relatively small, but it should be borne in mind that wood was scarce on the dune, and many of the flint tools could easily have been used held in the hand. It is not sure whether tar was used in the hafting of the flint axes. No remnants of possible tar were observed on their butt ends. But then it was probably not necessary to attach an axe to a haft with the aid of wood tar, as such implements were usually hafted by means of impact, and were at most held in place with fibres. Hafting with an adhesive was probably

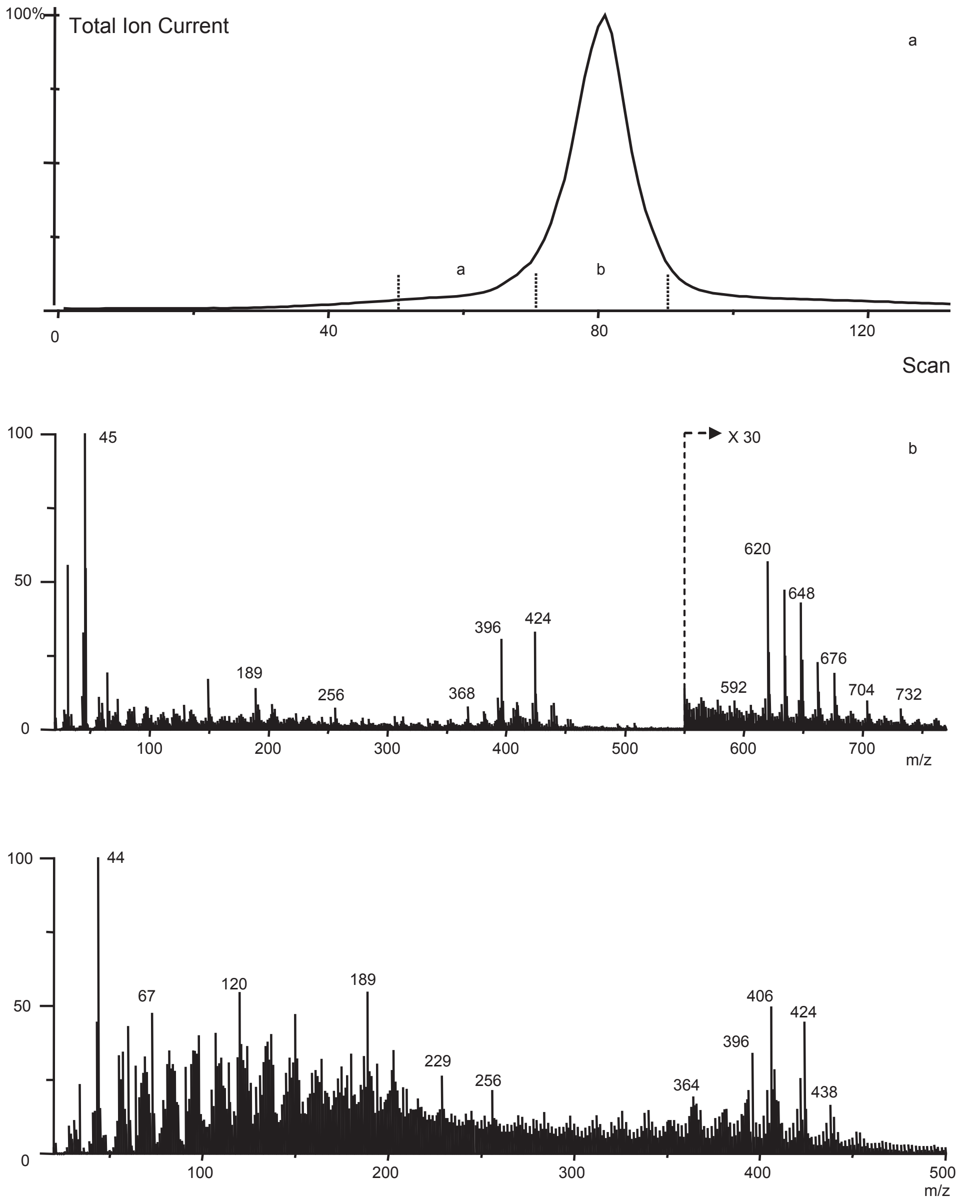

Figure 13.2 DTMS data of Schipluiden 8005 pitch sample showing a total ion current profile and the mass spectra summarised over in the scan ranges corresponding to evaporation of compounds (a) and thermally induced dissociation (b) leading to fragments of the cross linked pitch. The pattern of waxesters corresponding to beeswax is visible in the mass peak range from 590 to 740.

only relevant in the manufacture of arrows, and maybe incidentally in that of flake or blade tools.

Other uses have been proposed for tar, besides that as an adhesive (Aveling/Heron 1999; Pollard/Heron 1996). The chewing marks visible on this piece suggest that it served as chewing gum, possibly as a remedy for toothache. Tooth marks were observed on most of the pieces of tar found at Mesolithic sites in Scandinavia, as reported by Aveling and Heron (1999). To explain these ubiquitous tooth marks, they suggest that the tar was chewed to soften it prior to use, but they go on to argue that this is not very likely as saliva seems to diminish the adhesive qualities of tar. In four of the five cases analysed by Aveling and Heron the tooth marks are those of children aged 6-15. They note that this is the period during which children loose their milk teeth. This may well explain the tooth impressions observed on pieces of tar, but it does not exclude the possibility of the same material having been used as an adhesive, too. There is no reason why the birch bark tar should not have served multiple purposes.

The birch bark required to produce the tar was probably fairly readily obtainable. Birch may have grown in the catchment area of the Schipluiden occupants even though it is not represented among the wood and charcoal remains (chapter 21). The pitch could therefore have been produced locally, but we have no positive evidence to prove this. Being a very light, easily transported and preserved material, it may also have been brought to the site from elsewhere.

The practice of mixing resin with beeswax is known from ethnographic sources and has been studied in experiments (Van Gijn 1990). The relative amounts of resin and wax depend on the temperature: the higher the temperature, the greater the amount of resin that will be required, and the lower the temperature, the greater the amount of beeswax that will have to be mixed with it. Beeswax substantially enhances the flexibility of fixtures, as resin tends to be brittle. Birch bark tar is also very brittle without additives. Remains of beeswax have been found in ceramic vessels at various Middle Neolithic sites such as Bercy (Regert *et al*. 2001) and Chalain (Regert *et al*. 1999) and in the Middle Neolithic layers of the English site of Runnymede (Needham/Evans 1987). The authors who reported these findings attributed the presence of beeswax in the pots to its use as a sealant. The combined presence of birch bark tar and beeswax has recently been demonstrated in samples from ceramic sherds from Bronze and Iron Age contexts. The researchers interpreted this as the intentional mixing of birch bark tar and beeswax by Bronze and Iron Age peoples to obtain specialised adhesive products (Regert/Rolando 2002; Regert 2004). The lump of birch bark resin with beeswax admixture found at Schipluiden would push back the date of this specialised invention to the Middle Neolithic.[1]

The beeswax find has other implications as well. It indicates that the inhabitants of Schipluiden had access to honey to supplement their diet. Honey is rich in sugar, but it also has medicinal properties. The black honeybee *(Apis mellifera mellifera)* is indigenous in central and northern Europe, occurring as far north as Sweden and Norway (Millner 1996). It is highly adaptable to an adverse climate, will fly in drizzly weather and is capable of surviving harsh winters. It also forages over a long distance and is capable of surviving even where food resources are meagre (Millner 1996; T. Hakbijl, pers. comm.). There is no evidence to suggest that the honeybee had been domesticated by the time that the Schipluiden site was occupied, but the occupants may well have practised some sort of management of wild bee colonies. No lumps of birch tar were found in the contemporary assemblages of Ypenburg and Wateringen 4. Larger lumps of the fixing material have incidentally been found on tools, for example on one of the Sögel points from the Bronze Age barrow of Drouwen (Butler 1992). Small specks of possible tar have been observed on numerous flint tools during wear-trace analysis, also tools from Wateringen 4 (Van Gijn 1997). The Schipluiden find is however unique for this period. Such remains are very likely to be overlooked during excavation, as they resemble lumps of earth or clay. Usually a find like this leads to new finds, because people know what to look for. Whether this particular piece of tar was used as an adhesive or as chewing gum is not altogether clear. The teeth impressions do seem to point to the latter option. The presence of beeswax cannot be taken as proof that the wax was collected in the vicinity of the dune. It is equally possible that the inhabitants obtained the material

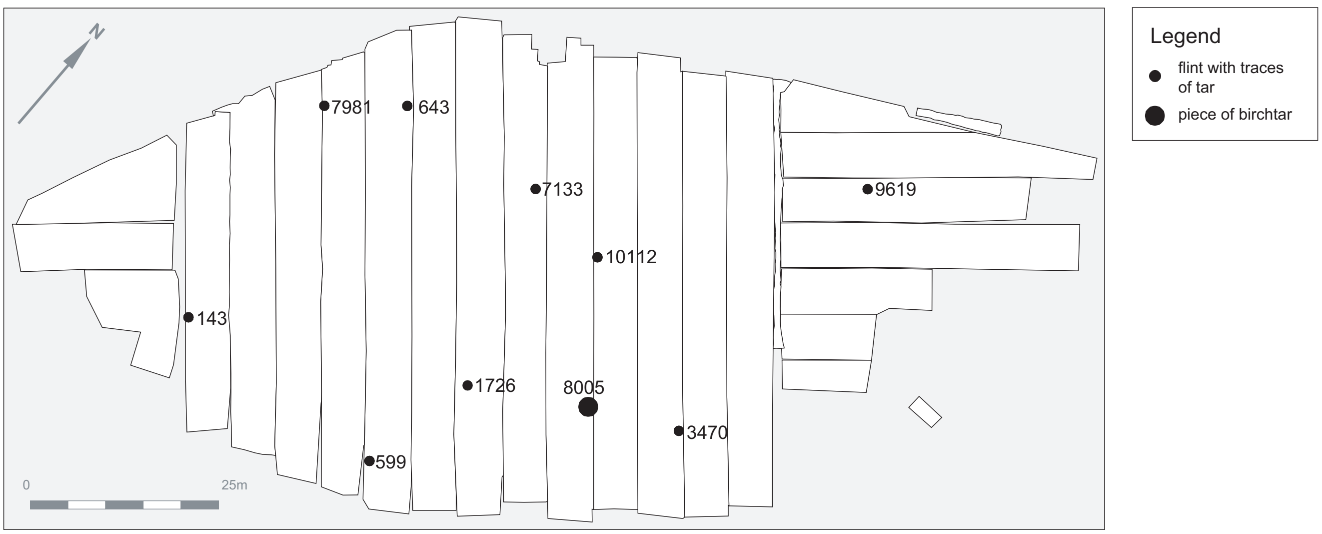

Figure 13.3 Findspots of the piece of birch bark tar and of flint with traces of tar.

from elsewhere. However, *Apis mellifera mellifera* is well adapted to fairly humid conditions, so there may well have been honeybees in the local environment. This would imply that honey could be exploited, too. Unfortunately bee remains are notoriously difficult to detect through entomological research due to their fragility and the unlikelihood of their remains ending up in a sample, but pollen analysis has proven successful in demonstrating beekeeping (Rosch 1999). The mixing of birch bark tar and beeswax had been demonstrated for Bronze and Iron Age contexts (Regert/Rolando 2002; Regert 2004), but the Schipluiden find indicates that this technological invention actually took place at least two millennia earlier, and probably has its roots in Mesolithic tool-making traditions.

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notes

1 The 1987 Needham and Evans article mentions the discovery of beeswax on a Neolithic sherd and dwells on the issue of beekeeping by prehistoric peoples. Interestingly, table 1 of this article includes a sample that was found to contain traces of beeswax alongside resin (sample S2). This same sample also contained traces of glucose, which is the focus of the authors' attention. They do not discuss the presence of resin in the sample, but this may actually be another indication that resin was mixed with beeswax at much earlier times than claimed by Regert/Rolando (2002), who associate this "invention" with the advent of iron metallurgy.

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