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DOI
10.1007/s12520-020-01179-y

Publication date
2020

Document Version
Final published version

Published in
Archaeological and Anthropological Sciences

Citation (APA)
Kozowyk, P. R. B., van Gijn, A. L., & Langejans, G. H. J. (2020). Understanding preservation and identification biases of ancient adhesives through experimentation. *Archaeological and Anthropological Sciences*, *12*(9), Article 209. https://doi.org/10.1007/s12520-020-01179-y

Archaeological and Anthropological Sciences (2020) 12:209
https://doi.org/10.1007/s12520-020-01179-y

ORIGINAL PAPER

Understanding preservation and identification biases of ancient adhesives through experimentation

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Received: 24 April 2020 / Accepted: 7 August 2020

Abstract
Adhesive production is one of the earliest forms of transformative technology, predating ceramics and metallurgy by over 150,000 years. The study of the adhesives used by Neandertals and early modern humans currently plays a significant role in debates about human technological and cognitive evolution. Depending on the type of adhesive used, different production sequences were required. These can vary in complexity and would have needed different knowledge, expertise, and resources to manufacture. However, our knowledge of this important technological development is severely hampered by poorly understood taphonomic processes, which affects the preservation and identification of adhesive materials and leads to a research bias. Here we present the results from a 3-year field preservation experiment. Flint flakes hafted and non-hafted with replica adhesives were left to weather naturally on and below the surface at two locations with different soils and climatic conditions. Differential preservation was recorded on a variety of natural adhesives by digitally measuring the surface area of each residue before and after the elapsed time. Residues were further assessed and photographed using metallographic optical microscopy. Results show that certain adhesives preserve to a significantly higher degree than others, while some materials may be more easily overlooked or visually misdiagnosed. We must therefore be aware of both taphonomic and identification biases when discussing ancient adhesive technology. This research provides a first look that will help us understand the disparities between which adhesives were used in the past and what we find in the archaeological record today.

Keywords Palaeolithic · Technology · Residue · Stone tool · Hafting · Experimental archaeology

Introduction

Adhesives and hafting have recently become the focus of intense study within the field of Palaeolithic archaeology. Compound adhesive production by Middle Stone Age humans in southern Africa, and hafting composite tools in general, is seen as evidence of complex cognition implying modern thinking earlier than previously thought (Barham 2013; Lombard 2007; Wadley 2005, 2010; Wadley et al. 2004, 2009; Wynn 2009). The production of birch bark tar by Neandertals has also featured in discussions about their technological knowledge and abilities, including their use and control of fire (Kozowyk et al. 2017b; Niekus et al. 2019; Roebroeks and Soressi 2016; Roebroeks and Villa 2011; Villa and Soriano 2010; Wragg Sykes 2015). A range of experimental work has provided further background knowledge on the material properties and the effects of fire on adhesive residues (Cnuts et al. 2017; Kozowyk et al. 2016, 2017a; Zipkin et al. 2014). Advances in chemical analyses have improved our ability to accurately identify adhesive types based on smaller and smaller residues (Cnuts et al. 2018; Hayes et al. 2019; Monnier et al. 2013, 2017, 2018). However, for all of this work, there are still a limited number of well identified and analysed adhesive residues on archaeological material of Palaeolithic origin.

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s12520-020-01179-y) contains supplementary material, which is available to authorized users.

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Currently, both securely dated and chemically identified Middle Palaeolithic hafting adhesives include material from just seven locations: Campitello Quarry, Fossellone and Sant'Agostino caves, Italy; Konigsaue, Germany; Zandmotor, the Netherlands, and Hummal and Um el Tlel, Syria (Boëda et al. 2008a; Degano et al. 2019; Hauck et al. 2013; Koller et al. 2001; Mazza et al. 2006; Niekus et al. 2019). Further evidence of Middle Palaeolithic hafting adhesives has been found, or inferred from use-wear, at a number of other sites (Cârciumaru et al. 2012; Hardy and Kay 1999; Pawlik and Thissen 2011; Rots 2009, 2013). However, precise chemical identification of residues is uncommon. Adhesive remains from the Middle Stone Age in Africa are similarly rare and include Diepkloof Rock Shelter (Charrié-Duhaut et al. 2013), Sibudu (Villa et al. 2015), and Border caves (Villa et al. 2012). Many residues lack secure chemical identification of organic remains and instead are inferred based on the presence of use-wear and/or inorganic residues, such as ochre, which is believed to have been a component of compound adhesives to improve strength (Kozowyk et al. 2016).

The limited number of adhesive finds from the Middle Palaeolithic and Middle Stone Age is problematic because of the significance adhesive production is given in discussions about Neandertal and early modern human technological and cognitive capabilities. The period from approximately 300,000 to 30,000 years ago was highly significant in human evolution. It is when *Homo sapiens* emerged, interbred with, and ultimately replaced two other hominin species (Galway-Witham and Stringer 2018). The same time period saw what is believed to be the first evidence of behavioural modernity (D'Errico 2003; Nowell 2010). Several significant technological developments also took place during this time. Prepared core technologies, such as the Levallois technique, became more widespread and allowed the production of smaller and sharper flakes of predetermined shape, also improving efficiency of raw material use and creating more uniform thickness (Lycett and Eren 2013). Further, the production and habitual use of fire by Neandertals is believed to have first occurred during the Late Middle Pleistocene (Roebroeks and Villa 2011; Sorensen et al. 2018). Fire provided light and heat necessary for cooking, giving warmth, and improving the properties of lithics (Clark and Harris 1985; Sorensen 2017; Wadley and Prinsloo 2014).

Flakes with a more uniform thickness are better suited to hafting, and the use of fire is a necessity for producing birch bark tar and mixing some compound adhesives (Kozowyk et al. 2017b; Wadley 2005). Together, these technological changes go hand in hand with the development of adhesives and hafting and provided an advantage to the prehistoric users over simple single-component handheld tools and naturally weak or brittle adhesives such as pure pine resin (Barham 2013; Kozowyk and Poulis 2019). However, the direct correlation between adhesives and other contemporaneous technological advances is still unclear. For example, was adhesive technology integrated with the earliest hafting, or did its use come later, after hafting was already well established? Uncertainties here are largely due to the poor preservation of organic materials in the Palaeolithic record. Further to this, the taphonomic impact on different adhesive types is as of yet unknown. The sensitivity of organic remains to these taphonomic processes combined with the highly variable nature of both natural adhesive materials and environmental conditions means that there is a high possibility of bias in the archaeological record. In addition, the successful discovery and identification of these materials is also minimized because knowledge about what environmental circumstances they survive in best is limited.

To address these issues, we have conducted a series of field preservation experiments. Flint flakes hafted with replica adhesives were left to weather naturally on and below the surface at the Leiden University Material Culture Studies experimental house at Horsterwold, the Netherlands; and the Forensic Anthropology Research Facility (FARF), Texas. The materials tested include pine tar, birch tar, pine resin, beeswax, acacia gum, hide glue, bone glue, and mixtures containing ochre and/or beeswax. We tested the influence of time, temperature, precipitation, soil pH, the influence of sediment cover, and adhesive types on residue preservation. Preservation was recorded by digitally measuring the surface area of each adhesive residue before and after the elapsed time. Microresidues were further assessed by stereo and metallographic microscopy and assigned a 'preservation index' score of between 0 and 5 (cf. Langejans 2010; Monnier and May 2019).

Materials

Organic remains in archaeology are broken down by three main forces: physical, chemical, and biological. The different properties of natural adhesives would suggest that they have highly variable preservation qualities, and some are much more likely to survive in the archaeological record than others. A number of adhesive materials and recipes have been tested here. Firstly, these include materials that are known to have been used during the Middle Palaeolithic in Europe: birch (*Betula)* bark tar, and pine (*Pinus*) resin (Degano et al. 2019; Mazza et al. 2006). Secondly, the materials demonstrated by the Middle Stone Age in southern Africa, including compound adhesives of conifer resin, beeswax, and ochre, were investigated (Charrié-Duhaut et al. 2013; Lombard 2006; Villa et al. 2015; Villa et al. 2012). Thirdly, we included some materials that would have been present and readily accessible but that have never been chemically identified in the Pleistocene archaeological record, such as acacia gum.

Lastly, hide and bone glue were studied, as these are materials that are known to have been used in historical times, but are not common in prehistory, although the technology required to produce them did exist.

Tar

Tar is a dark viscous liquid material obtained from the pyrolysis or gasification of biomass. The term 'pitch' is commonly used to refer to materials made from the pyrolysis of woody materials and more accurately represents such material that is solid at room temperature (Betts 2000). However, pitch is also sometimes used to refer to pine wood extractives such as gum rosin (Langenheim 2003) and to heated/treated pine resin (Odegaard et al. 2014). So to avoid confusion, for the purpose of this article, we will use the term 'tar' throughout to refer to the material produced from the pyrolysis of plant materials, whether solid or liquid at room temperature.

The oldest known adhesives ever recovered (> 191 ka) come from Campitello Quarry in central Italy and have been chemically identified using GC-MS as being birch bark tar (Mazza et al. 2006). Two more lumps of birch bark tar have been found at the open-pit mine of Konigsaue, Germany. These have been chemically identified using GC-MS and are minimally dated to approximately 40,000 years ago (Koller et al. 2001). A single lump of birch tar adhering to a flint flake has also been found from the Dutch North Sea. This piece has been chemically identified by py-GC-MS and directly AMS 14C dated to approximately 50 ka (Niekus et al. 2019). Black residues have been identified on a number of flint tools from Inden-Altdorf, Germany, and Sterosele, Ukraine. Although no chemical analysis has been done, they are believed to be birch bark tar (Hardy and Kay 1999; Pawlik and Thissen 2011). Birch tar adhesives have also been identified at a number of Mesolithic and Neolithic sites (Aveling and Heron 1998; Aveling and Heron 1999; Regert 2004; Urem-Kotsou et al. 2002; Van Gijn and Boon 2006), making it the most commonly identified prehistoric adhesive in Europe.

Despite the apparent bias in favour of birch bark as a material to make adhesives from during prehistory, tar can be produced from any organic material by the same process. Pine tar has been identified in the Greek Neolithic (Mitkidou et al. 2008), and in historic times, pine wood was a primary source of biomass for tar production (Kunnas 2007). It was produced on an industrial scale in Scandinavia and Finland for use as caulking in ships and waterproofing or preserving wood on church roofs (Connan and Nissenbaum 2003; Egenberg et al. 2003; Kunnas 2007) and is still being manufactured today for a number of different purposes (Kurt et al. 2008; Lopez et al. 2010; Paghdal and Schwartz 2009). Both birch and pine species of trees were present together from the end of MIS 6 until MIS 1 and the beginning of the Holocene (Helmens 2014). Although pine tar has been used for waterproofing and protecting wood, birch bark tar is well known for its antimicrobial and antibacterial qualities (Baumgartner et al. 2012; Yogeeswari and Sriram 2005). Early birch tar may even have been used as a treatment for toothache (Aveling and Heron 1999; Van Gijn and Boon 2006). These properties may result in better preservation, and thus a bias in the archaeological record.

To make tar for our experiments, we used a modified gas pottery kiln with an apparatus to allow the heating of wood or bark in an oxygen reducing environment. A 1000-mL metal container with a sealable lid was filled with 193.0 g of pine (*Pinus sylvestris*) wood and another with 110.0 g of birch (*Betula pendula*) bark. After 2–3 hours between 350 and 405 °C, the pine wood produced 55.5 g of extractives and the birch bark produced 40.8 g of extractives. These were reduced over a hot plate to remove the volatile portion and produce a material with a consistency that was solid at room temperature (cf. cf. Kozowyk et al. 2017a). After this, 14.5 g of wood tar remained (7.5 % yield by weight) and 17.55 g of birch tar remained (16.0 % yield by weight).

Resin

Resins are a form of plant exudate present in the resin canals and excreted at points of injury to help prevent infection and biological damage in trees (Sjöström 1981). They are made primarily of monoterpenes and resin acids (Silvestre and Gandini 2011). Unlike tar, which must be chemically transformed from a material that does not resemble the finished product, resin occurs naturally in a sticky form. Resin is also commonly found in archaeology associated with hafting. The oldest chemically identified adhesive for hafting from the Middle Stone Age is a conifer resin from the yellowwood (*Podocarpus*) tree (Charrié-Duhaut et al. 2013). Pine resin has also been identified in a Middle Palaeolithic context in Italy (Degano et al. 2019).

Today, resin is most commonly harvested from various pine species by cutting V-shaped notches in the trunk and collecting the resin (or oleoresin) as it flows from the tree as a clear viscous fluid. Resins harvested from pine are often refined further to produce rosin, also referred to as colophony (Fiebach et al. 2005). Rosin is brittle, glassy, transparent solid that is non-volatile and insoluble in water (Coppen and Hone 1995) and is obtained by removing the volatile turpentine or pine oil portions that may be present in resin (Gaillard et al. 2011).

If, as would be the case during prehistory, the method of extraction was collecting resin from a wounded tree, as opposed to chemically extracting it from pine wood, it could be found in a range of different consistencies. When fresh, oleoresin contains approximately 68% rosin, 20% turpentine, and 12% water (Gidvani 1946). It is sticky to the touch but also very soft. As the turpentine and water evaporate, the ratio of rosin increases and the material becomes harder and more brittle. In order to improve replicability, and to avoid uncontrollable variables, we are using store-bought pine *rosin* for our experiments. However, when referring to archaeological material, we will continue to use the term *resin*, as it is unknown whether prehistoric people were using it in a fresh, more 'resinous' state, distilling it into rosin, or collecting it when it was already dry and brittle. It is generally accepted that pure rosin makes a poor and brittle adhesive and requires additives or plasticizers to make it useable (Gaillard et al. 2015). However, there are examples where resin may have been used without any additives or where it may have been advantageous to have a brittle material (Ellis 1997; Nelson 1997; Wadley et al. 2015). The state of the resin when collected may have influenced the necessity to add plasticizers or mineral additives to alter the physical properties—such as increasing stiffness and reducing drying time of resin with ochre or improving plasticity and workability of rosin with beeswax or fat (Wadley 2005, 2010).

The rosin in this study was heated over an electric hotplate and applied in a molten state to the flint and haft. For compound adhesives, 30 wt.% beeswax was melted and mixed in, and 20 wt.% ochre was then added, as this was determined to be the optimum ratio in adhesive shear tests (Kozowyk et al. 2016).

Gum

Gums are similar to resins in that they are plant exudates formed within a tree and excreted at points of damage in order to aid healing and inhibit infection (Coppen 1995). Visually and physically, gums can be almost indistinguishable from resins. They are both exuded from trees as a transparent sticky viscous liquid, and they both harden and become more brittle as they dry on exposure to the air and sun. Gums differ in that they are composed primarily of sugars and are water-soluble (Langenheim 2003). Archaeological experimentation has shown that acacia gum (also known as Gum Arabic) can be used as a successful adhesive but that the properties can be highly variable and often require additives such as ochre to improve the workability and alter the performance (Wadley 2005; Zipkin et al. 2014). Gums have been used as adhesives in more recent times (Mason et al. 1891) and would have been available to ancient humans living in southern Africa. Gum exuding trees are widespread, with acacia alone being present throughout Africa, Arabia, portions of Iran, India, Australia, southern United States, and Central America (Mantell 1954). Possible evidence of gum adhesives on Uluzzian backed segments has recently been identified at Grotta del Cavallo, Italy (Sano et al. 2019). The absence of any identified gum adhesives from the Pleistocene is then unlikely to be due to economic, technological, performance, or environmental factors. The solubility in water and sugar-rich chemistry of gums suggest another alternative. They are much more chemically and biologically susceptible to degradation than resins and tars. To apply our store-bought acacia gum adhesive, we first crushed and then re-constituted it with water until a thick, sticky paste. Then we applied it and left the gum to air dry.

Animal glues

Animal glues represent a different form of adhesives than plant exudates and tars. They are produced by removing the collagen from organic animal remains, namely, animal or fish bones, or animal hides, and converting it through hydrolysis into a natural polymer. This requires a considerable investment in time and energy but is otherwise not an overly complicated process (Pearson 2003). Collagen extract is collected by boiling the animal remains in water for a prolonged period; through a process of denaturation, the collagen is converted into gelatin (Schellmann 2007). Hide and bone glue today are primarily made of bovine hides and a mix of bones from cattle and pigs (Schellmann 2007). The earliest recognized use of hide-based glues occurs in ancient Egypt and Mesopotamia, where it was likely employed for a range of purposes including fastening wood together, applying ebony and ivory inlay, fastening woven fabric to wood, and glueing gold foil to plaster (Lucas and Harris 2012; Moorey 1999). No finds are known elsewhere, with the exception of a rare Neolithic find from Switzerland, where it was used in a composite bow (Bleicher et al. 2015). Animal glue use has also been documented among Native Americans in North America for tasks such as glueing feathers to arrow shafts or composite bow manufacture (Campbell 1999; Mason 1894). Until the advent of synthetic polymer glues in the 1950s and 1960s, animal glues were the material of choice for woodworking, carpentry, book binding, paper making, and many other tasks (Duhamel du Monceau 1771; Hull and Bangert 1952; Keystone 1934; Pearson 2003). To be used, animal glues are soaked in warm water and heated to just below boiling temperature. The virtual monopoly animal glues had over all other types of natural adhesives in the last several centuries raised the question of why it was not used more often in the deep past? Was it unknown prior to the Neolithic? Was it unnecessary to invest so much time in manufacture when natural and 'ready-to-use' plant adhesives would work? Or does the water-soluble nature disfavour preservation in European prehistory outside of truly exceptional circumstances?

To obtain insight into this question, hide and bone glue adhesives were prepared using methods still employed in some traditional furniture and musical instrument manufacturing today (James 2011; Joyce 1987). Water is added to the dried adhesive pellets, which become gel-like. Then they are heated inside a second pot of water, to avoid overheating, until the adhesive liquefies. Once liquid, it can be applied to the haft and flint flake and left to dry.

Beeswax

Beeswax is a natural wax produced from a number of different types of bees, one of the most common being *Apis mellifera*. It consists primarily of hydrocarbons (14%), monoesters (35%), diesters (14%), free acids (12%), and many other components, although these amounts vary slightly depending on the species of bee and the wax's origin (Tulloch 1980).

Beeswax is used as a component in compound adhesives containing resins and possibly gums (Sano et al. 2019). At low temperatures beeswax is brittle, but at room temperature it becomes relatively soft and so it is frequently mixed with resin to act as a plasticizer and soften the otherwise brittle material (Gaillard et al. 2015; Kozowyk et al. 2016). The oldest identified beeswax use comes from Border Cave, South Africa, and dates to approximately 44 ka (Wadley et al. 2015). Beeswax may also have been used at Fossellone Cave (Degano et al. 2019) and Grotta del Cavallo, Italy (Sano et al. 2019). More modern beeswax was found on a Final Palaeolithic barbed point from Bergkamen, Germany (Baales et al. 2017), and it is likely that by the Neolithic, the honeybee was being widely exploited (Roffet-Salque et al. 2015; Van Gijn and Boon 2006). For our experiments, we used commercially available pure beeswax and applied it to the flint in the same manner as the resin adhesives.

Ochre

Ochre is a general term often used to refer to natural clay earth pigments obtaining their colour from different iron oxides but may be broadened further to include any mineral substance containing iron oxide (Rifkin 2011). Ochre, like beeswax, is used primarily as an additive in compound adhesives. On its own, ochre has no adhesive qualities, so its use in hafting has raised some debate over a possible symbolic or technical nature (Wadley 2010). Ochre has been shown to improve the performance and ease of use of resin-based adhesives (Kozowyk et al. 2016; Wadley 2005). However, it is also possible that other clay-like sediment without the iron oxide component of ochre may serve a similar function (Zipkin et al. 2014). Ochre has been identified in many instances with a direct correlation to hafting, dating back to the Middle Stone Age, so its use is unambiguous, regardless of its purpose (Allain and Rigaurd 1989; Bradtmöller et al. 2016; Dickson 1981; Helwig et al. 2014; Lombard 2006; Sano et al. 2019; Shaham et al. 2010; Villa et al. 2015).

The significance of ochre in debates about symbolism (Hovers et al. 2003) and the technical knowledge or skill of early modern humans make it necessary to better understand taphonomic processes affecting ochre-containing adhesives. The relatively high proportion of ochre-hafting relationships in the current literature raises some questions about its abundance in prehistory. Was ochre frequently and actively sought out as an ingredient in adhesives? Or is the high number of documented cases due to research and taphonomic biases? Ochre may have some antibacterial/microbial properties that help reduce the biological decay of hides (Rifkin 2011). Does this lead to an increase in preservation of residues over non-ochre-containing adhesives? Does the distinctively red appearance of ochre simply mean that it is identified by archaeologists more frequently? It must also be noted that the presence of ochre is not necessarily linked with adhesive use. It may also be added for symbolic reasons (cf. cf. Rifkin 2015). The purpose of including ochre in gum and resin adhesives in this study is to determine if its presence improves the successful identification of hafting residues either by increasing visibility or by providing some form of biological protection.

With the exception of pine tar and birch bark tar, all adhesive materials were purchased from https://www.verfmolendekat.com/en/webshop/. The ochre used in this study is pre-ground to a fine particle size (< 62.5 μm) as this has been reported to produce a strong adhesive (Zipkin et al. 2014).

Methods

Flint flakes hafted with replica adhesives were left to weather naturally on and 10 cm below the surface at the Leiden University Material Culture Studies experimental house at Horsterwold, the Netherlands and the Forensic Anthropology Research Facility (FARF), USA. Differential preservation was recorded by digitally measuring the surface area of each adhesive residue before and after the elapsed time. We opted for field experiments because they mimic real situations when artefacts are discarded and include a combination of biological, chemical, and physical decay.

Field preservation

Adhesives are known to have been used for hafting in Europe as far south as Italy and north as the North Sea (Mazza et al. 2006; Niekus et al. 2019), as well as throughout Africa (Lombard 2006; Rots et al. 2011) and the Levant (Boëda et al. 2008b). The range of burial environments in which archaeologists might find adhesive residues is therefore vast. For this study, field preservation experiments were conducted at two highly different locations in order to reflect as broad of a spectrum of potential burial environments as possible. While the locations are not intended to replicate any specific archaeological site, results will provide information on whether burial environment or adhesive type has a greater effect on the preservation potential of residues. Variation in burial environment will also help illuminate any potential differences that might exist between adhesive types.

Field preservation experiments are broken down into four main categories based on the geographic location and the object location and are then further subdivided based on duration:

1. Objects on the surface at the Horsterwold Experimental House, the Netherlands
2. Objects buried 10 cm below the surface at the Horsterwold Experimental House
3. Objects on the surface at FARF, USA
4. Objects buried 10 cm below the surface at FARF, USA

A total of 160 10-mm diameter pine wood dowels were notched and joined with 10 different replica adhesives to Rijkholt flint flakes in a cleft haft. Half of the hafted samples were removed after 0.5 years ($n = 20$) and the other half after 2 years ($n = 20$) at FARF and 0.5 years ($n = 20$) and 3 years ($n = 20$) at Horsterwold. At the Horsterwold location, a further 28 samples were made by applying adhesives to the surfaces of larger flint flakes, without using hafts. Of these, 14 were buried for 3 years, and 14 were left on the surface for 3 years. Each material and location was tested in duplicate. Once excavated and collected after the elapsed time, the objects were lightly rinsed with distilled water to clear away excessive sediment, and left to dry for several days before being photographed, measured, and observed with an optical microscope (Fig. 1).

Environmental conditions

Climate conditions at FARF near San Marco, Texas, and Horsterwold near Zeewolde in Flevoland, were taken from 'World Weather Online' https://www.worldweatheronline.com. Monthly conditions are recorded for maximum, minimum, and average temperature, rainfall and rainy days, humidity, and UV index for the period of April 2016 to May 2019. The area of the facilities in Texas experiences a wide variation in temperatures and conditions, indicating a humid subtropical climate. The temperature is hot, with humid summers and short cool winters and significant rainfall variation throughout the year. During the course of these experiments, FARF experienced several storms with flashflooding and heavy rainfall. The climate conditions at Horsterwold, the Netherlands, are milder, with cool summers and temperate winters. Rainfall is fairly evenly distributed throughout the year. Below is a comparison of the monthly temperatures and precipitation during the period of July 2016–July 2017, when experiments were active at both locations (Fig. 2).

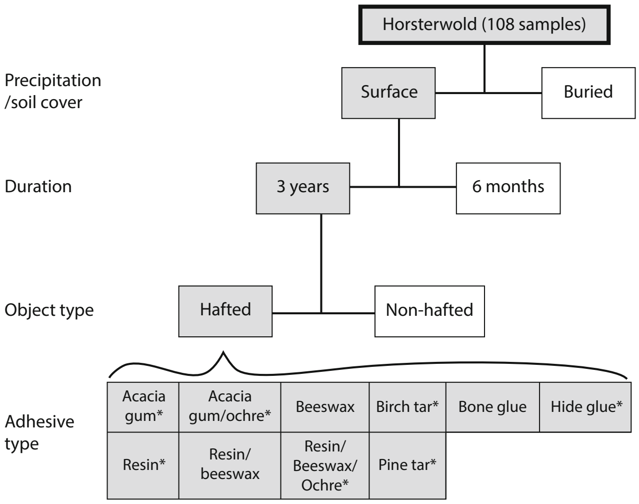


Fig. 1 Organization chart of the experiments conducted at Horsterwold. Experiments were the same at FARF and the chart is symmetrical (e.g. experiments are the same for both surface and buried). Each adhesive type was tested in duplicate. *Only these adhesives were tested for 3 years at Horsterwold on non-hafted flakes

Soil samples were taken from approximately 1 meter away from the adhesive samples to measure the soil pH levels. Analysis was done using an Accumet AB150 pH/mV (cf. cf. ASTM 2019). Soil pH from two Horsterwold samples are 7.44 and 7.46. Horsterwold soil is a mixture of fine loamy sand and clay from the reworked Pleistocene sands. The immediate location was dredged from the nearby area to create a small artificial island on which the experiments took place. Vegetation at Horsterwold is primarily a deciduous woodland with thick grass growing near the sample locations. Soil pH from two FARF samples are 6.41 and 6.33. The soil at FARF is shallow stony clay over hardened limestone, providing limited storage for water and a high inorganic carbon content reducing plant growth (Carson 2000). The vegetation at FARF is perennial grassland. Samples were buried at both locations in soil horizon A.

Macroscopic assessment and optical microscopy

In order to quantify the residue preservation, a 'preservation index' from 1 to 5 was used (Langejans 2010; Monnier and

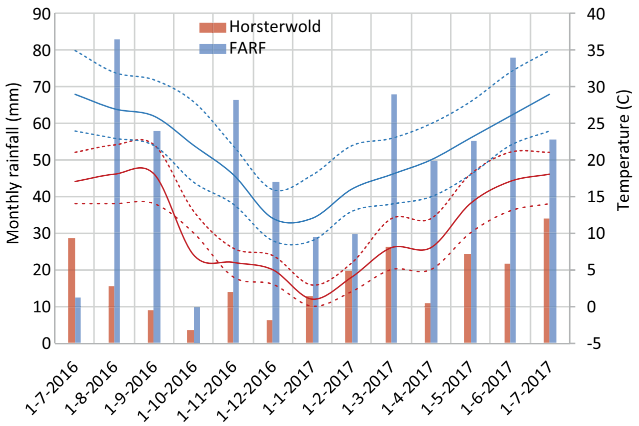


Fig. 2 Monthly average weather for Horsterwold and FARF. Bars = monthly rainfall, solid lines = average monthly temperature, dotted lines = max and min monthly temperatures

May 2019). Different materials will preserve in different ways, so the scoring used in this paper is unique to adhesives but provides a simple comparative tool to understand the relative preservation of different residues (Table 1).

Preservation was further recorded for macro-residues by photographing and digitally measuring the surface area of each adhesive residue before and after the elapsed time. This was done with the measurement tool in Adobe Photoshop CC 2018 19.1.5. Due to the variety in colours, contamination with soil, and translucency of some adhesives, automatic measurements could only be conducted for some red residues from the ochre-containing adhesives. This also precluded the use of image measurement software such as ImageJ. However, a test automatic measurement using the histogram setting in Photoshop on one red ochre-containing adhesive gave a result within 2% of the manual measurements. On objects where no clear residues were visible macroscopically, the flint surface was scanned under a metallographic microscope at × 40 magnification, and any potential residues were recorded.

Results

The results are first divided into two main categories based on the location of the experiment: those conducted at Horsterwold in the Netherlands and those conducted at FARF in the USA. They are then further divided into those experiments left to weather on the surface and those buried 10-cm underground. Six-month experiments are summarily discussed to understand the initial decay. Due to the short duration, they are not further elaborated on as we consider the long-term preservation to be most relevant for archaeological remains. At the Horsterwold location, a total of seven objects were not recovered from all surface experiments and two objects were not recovered from all buried experiments. This suggests that the surface samples were more easily disturbed by physical activity and may have been moved by water flow or animal and plant activity. A total of 13 FARF samples were not recovered due to several extreme flash floods which took place during the allotted time.

Horsterwold results

Surface

After a period of half a year, the distinction between water-soluble and non–water-soluble materials is immediately apparent (online resource Table 1). Acacia gum, hide glue, and bone glue all have a preservation index of zero. Acacia gum with ochre has a preservation index of 3, because there were traces of ochre found across the hafted surface. At the other end of the scale, pine tar, birch tar, beeswax, and resin/beeswax/ochre all received scores of 5 because large amounts of residues remained nearly completely resembling the adhesive when it was freshly applied. Pine resin and pine resin/beeswax received scores of 4 and 4.5, as slightly less residue remained. Recording the precise surface area of residues remaining shows a slight hierarchy of preservation potential of the non–water-soluble adhesives. Resin/beeswax/ochre and birch bark tar both preserved to around 100%. Further, these remains spread out to take up a larger surface area than when deposited. On average, beeswax remained over 96% of the original surface area, pine tar over 93%, resin/beeswax over 92%, and resin over 79% of the original surface.

After 3 years, the difference between water-soluble (gum, hide, and bone glue) and non–water-soluble (resin, beeswax, tars) is still a clear distinguishing factor between adhesive types, as would be expected. While many of the non–water-soluble adhesives in the hafted objects still preserved to a relatively high degree, often with > 75% of the original residue remaining, differences in the amount of remaining surface area are more apparent than after half a year.

The preservation indices on non-hafted flint flakes are lower than hafted flakes (online resource Table 2). Pine tar scored an average index of 4.5 when hafted and 2 when left on the surface of a non-hafted flake. Birch tar lowered slightly from an average index of 5 to 4.5. Pine resin remained the same, and pine resin/beeswax/ochre scored 5 while hafted and 4 on

Table 1 Preservation index of adhesive residues, after (Langejans 2010)

Preservation index					
5	4	3	2	1	0
Situation just after use. Thick residue adhering to the flint over > 90% of the original covered surface	Abundant presence of macro-residues over < 90% of the original covered surface	Small traces of macro-residues or considerable discolouration or staining left from the adhesive	Few deposits left, difficult to see macroscopically. Only slight discolouration or staining on the flint surface	The occasional residue left. Visible microscopically, usually in flake scars or protected surfaces on the flint	No observed residues left

non-hafted flakes. Acacia gum/ochre scored 3 while hafted and an average of 1 when non-hafted (online resource Table 2).

Buried

After a period of half a year, results of the buried samples were similar to those on the surface (online resource Table 3). With the exception of one bone glue sample, which showed very small trace residues (score of 1), acacia gum, hide glue, and bone glue all have a preservation index of zero. Acacia gum with ochre has an average preservation index of 3.5, because there were substantial traces of ochre found across the hafted surface. Pine tar, birch tar, pine resin, beeswax, resin/beeswax, and resin/beeswax/ochre all received scores of 5 because large amounts of residues remained, nearly completely resembling the adhesive when it was freshly applied.

After 3 years, birch tar appeared almost unaltered and in two cases spread out to cover a larger surface area than when it was first applied, with an average preservation index of 5 for both hafted and non-hafted flakes (online resource Table 4). Pine tar, on the other hand, appeared more heavily degraded (preservation index of 4.5 for hafted flakes and 3.5 for non-hafted flakes). Although much of the residues were still there, the colour had become more brown, and the surface was cracked and flaking. On the buried samples, there was still a slight difference between adhesives used with a hafted flake and adhesives which were on a non-hafted flint flake. The non-hafted flakes preserved residues to a slightly lower degree. As with the other experiments, almost no residues were identified securely from the water-soluble adhesives. One exception is the acacia gum and ochre adhesives, which left some slight staining and discolouration over the hafted area, giving an average score of 2 for hafted flakes and 1.5 for non-hafted flakes. It is unlikely much of the organic gum preserved; however, it does provide a clear indication of the region of the tool that was hafted.

On average, the preservation index of the buried experiments does not differ much from the surface experiments, although the non–water-soluble adhesives appear to have preserved slightly better when buried (Fig. 3). The average preservation index for hafted adhesives is higher than non-hafted samples for non–water-soluble adhesives. For example, buried birch tar = 5, surface birch tar = 4.5, buried pine tar = 3.5, surface pine tar = 2, and buried acacia gum/ochre = 2 while surface acacia gum/ochre = 1.5. Scores for resin/beeswax/ochre and resin are equal for buried and surface samples (Fig. 4). Comparisons are more difficult with water-soluble adhesives, because preservation is so poor that accurate identification with optical microscopy is problematic. However, it is clear that the addition of ochre greatly increases visual identification potential of organic adhesive residues.

FARF results

Surface

After half a year on the surface at FARF, patterns of preservation reflect those at Horsterwold; however, no non-hafted flint flakes were tested here, so comparisons with these cannot be made. Birch bark tar preserves the best, and acacia gum, hide glue, and bone glue preserve poorly (online resource Table 5). However, already after 6 months, there is a greater disparity among the preservation of adhesives than at Horsterwold. Birch tar and resin/beeswax/ochre were the only adhesives with a preservation index of 5 after half a year on the surface. The next best preserved were resin/beeswax (4), then pine resin (4), and pine tar (3.5). Acacia gum/ochre scored the same as beeswax (3), because it was easily identifiable and a large portion of the original surface area was stained red.

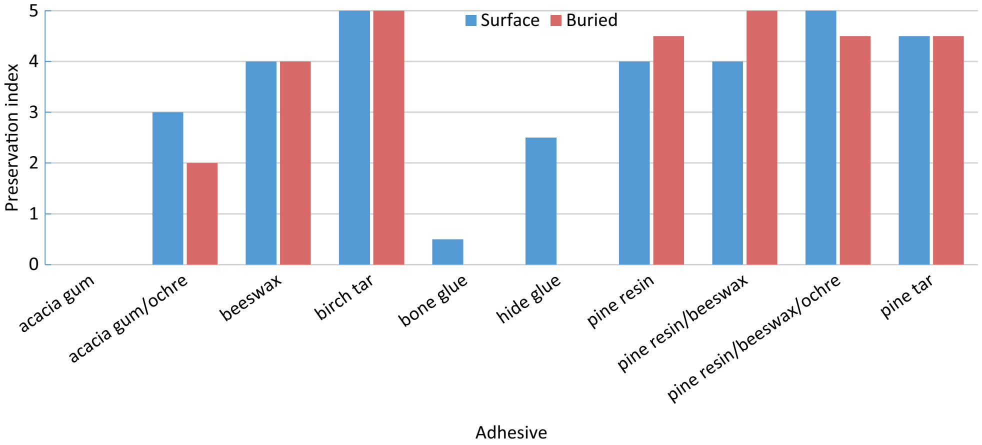
After a total of 2 years, the surface residues at FARF changed very little. Birch bark tar still appeared fresh and spread out to cover a slightly larger surface area than when first applied (score of 5). Resin/beeswax/ochre has the second highest preservation index (4.5), followed by resin/beeswax (4), resin (4), beeswax (3), acacia gum/ochre (3), hide glue (2), bone glue (1), and acacia gum (1; online resource Table 5).

Buried

After half a year at FARF, the buried samples preserved to a slightly higher degree than the surface experiments (online resource Table 6). Birch tar preserved the best; however, in these experiments one of the pine tar samples, as well as pine resin, resin/beeswax, and resin/beeswax/ochre also all scored a preservation of 5. In the order of decreasing preservation index, the remaining buried adhesives were acacia gum/ochre, hide glue, bone glue, and acacia gum.

After 2 years, the preservation index remained slightly higher for adhesives that were buried compared with adhesives that were left on the surface, although fewer samples were recovered from the experiments with buried adhesives, so the difference is minor. Birch tar preserved the best (5), appearing almost unchanged since its application. Resin/beeswax/ochre preserved similarly well (5), and resin/beeswax (4.5) preserved third best. They were followed by pine resin (4), beeswax (3.5), pine tar (3), acacia gum/ochre (3), hide glue (2), and finally acacia gum (1). Bone glue samples were not recovered from this location (Fig. 5).

Fig. 3 Average preservation index of adhesives on hafted flint flakes after 3 years at Horsterwold



Discussion

Discussion of results

Overall, the preservation of adhesive residues is determined primarily by the type of adhesive and, then to a lesser extent, by the presence of a haft and by the environment. Adhesives on hafted flakes preserve better than on non-hafted flakes and appear to preserve similarly at both Horsterwold and FARF. Being on the surface or buried has little effect on preservation. Adhesives that are non–water-soluble preserve better than water-soluble adhesives. Birch tar preserves exceptionally well, often appearing similar or spreading out to a larger area than when first applied (Fig. 6). Pine resin preserves surprisingly well given resin's brittle nature. For example, on non-hafted flakes, pine resin had a preservation index of 4 for both buried and surface samples, while pine tar had a preservation index of 3.5 and 2, respectively. A combination of beeswax and resin preserves significantly better than beeswax on its own (two-tailed *t* test with independent means for all hafted samples: $t = 3.18$, $p = < 0.01$). The difference between resin and resin/beeswax is less clear based on the amount of residue remaining; however, many of the pure resin adhesives were more fragile and prone to losing pieces during handling. The addition of ochre likely improves the preservation of resin/beeswax adhesives. Ochre has no recognizable protective properties when added to acacia gum; however, it often remains highly visible while the gum disappears. After 2 years, ochre can also move and be deposited on areas not originally covered by the adhesive (Fig. 6).

When looking at only those adhesives which had the highest preservation potentials, it is helpful to directly compare the percentage of adhesive residue remaining (Fig. 7). When considering all hafted adhesives, buried, and surface from both locations, birch bark tar falls well outside of the range of standard error of the other adhesives and preserves to a significantly higher degree than resin/beeswax/ochre (two-tailed *t* test with independent means: $t = 4.12$, $p = < 0.01$) or pine tar ($t = 3.55$, $p = < 0.01$). Among the other materials, the difference is not so pronounced. However, resin/beeswax/ochre preserved more consistently well than the others. It also clear that beeswax on its own does not survive as well as some of the other materials.

Fig. 4 Average preservation index of adhesives on non-hafted flint flakes after 3 years at Horsterwold

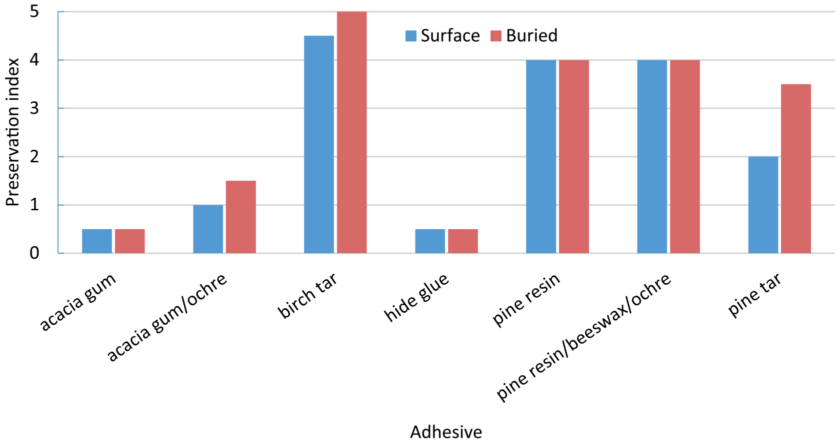
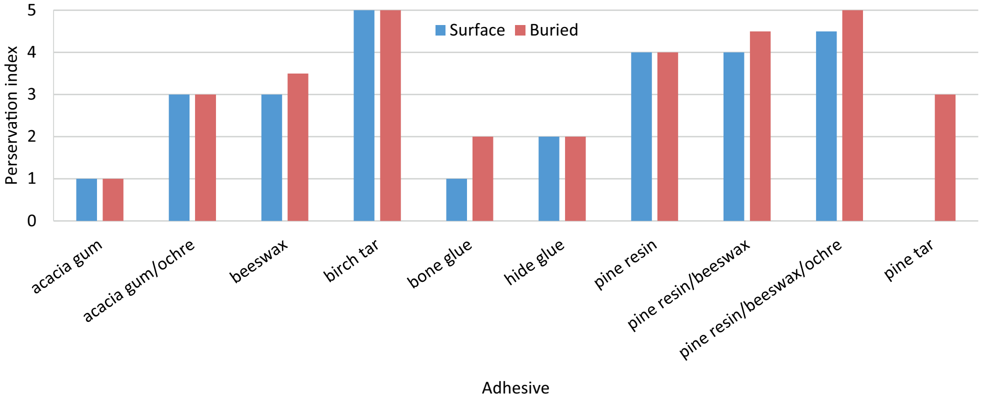


Fig. 5 Average preservation index of adhesives on hafted flint after 2 years at FARF. Surface pine tar samples were not recovered



Several adhesives that preserved relatively well on hafted tools appear to have survived to a lesser degree on non-hafted flakes (Fig. 8). Likewise, in the single instance where birch bark tar preserved poorly (49% residue remaining), it was on a non-hafted flake on the surface (Fig. 8f). As the wooden handles appear to have offered some protection, when tools are removed from hafts, either accidentally or intentionally, the likelihood that residues will preserve is further decreased. This has potentially significant ramifications for determining how many tools were hafted in an assemblage, as any tool that was removed from a haft during its use life is less likely to preserve evidence of the adhesive used. Unfortunately movement of many of the surface samples by heavy rainfall meant that we were unable to determine whether preservation was affected by the residue being on the upper or lower side of the tool.

Environmental factors influencing adhesive preservation

After 3 years at Horsterwold, preservation of hafted non–water-soluble adhesives was slightly better than after 2 years at FARF. The pattern appears reversed for water-soluble adhesives, but this may be attributed to difficulties in the accurate identification of the micro-remains of these materials. The increased decay at FARF is therefore likely due to the environment.

Rates of decay are highly influenced by temperature (Hollesen and Matthiesen 2015). Further, many of the adhesive materials tested also significantly soften at temperatures of around 40 °C (Kozowyk and Poulis 2019). Chemical weathering is also limited in the absence of water, which

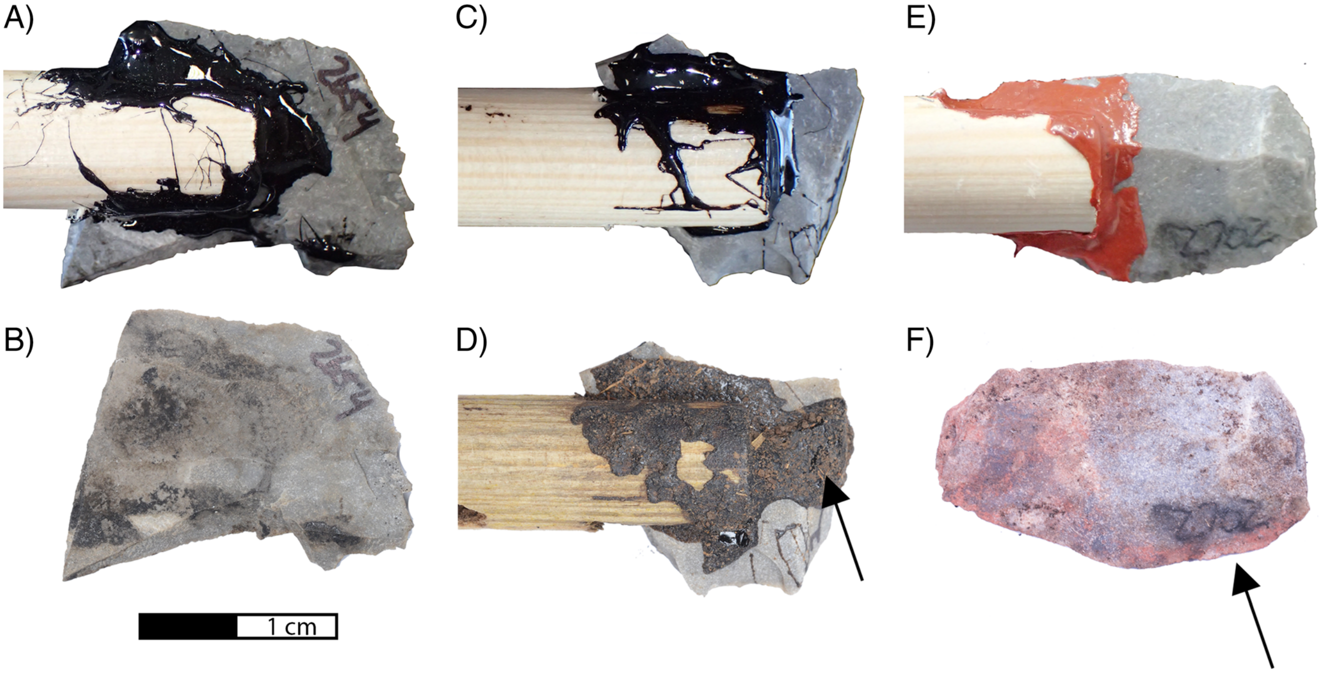


Fig. 6 Image showing spreading of adhesive residues after deposition. Residues before and after of pine tar buried at FARF for 6 months (A, B); birch tar buried at FARF for 6 months (C, D); gum/ochre from the surface at FARF for 2 years (E, F). Arrows point to portions of adhesive residue that have expanded over areas of the flake not originally covered by adhesive

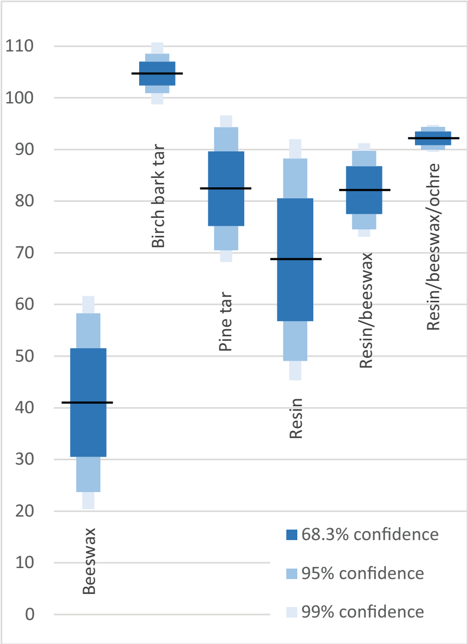


Fig. 7 Bullet graph displaying the error ranges for beeswax, birch tar, pine tar, resin, and resin/beeswax and resin/beeswax/ochre adhesives. Birch tar falls well outside the 99% confidence interval of the other adhesives

carries away by-products of decomposition (Chesworth 1992; Langejans 2010). A combination of hot and humid temperatures and heavy rainfall at FARF will therefore lead to increased biological decay, as well as increased mechanical decay and erosion. On the other hand, although pH levels are close to neutral, they are slightly more alkaline at Horsterwold and acidic at FARF. Microbial biomass increases with pH between 6 and 8 (Aciego Pietri and Brookes 2008), suggesting microbial activity might be higher at Horsterwold. Soil at both locations consists of clay, yet there is more sand at Horsterwold, which has two potential contrasting effects. Firstly, studies have shown that microbial biomass is most concentrated in finer-grained silt and clay soil fractions (Sessitsch et al. 2001). Secondly, larger grain size increases the flow of water (Allison and Bottjer 2010), which facilitates decay. As the differences in pH and soil grain size are relatively small between both locations, the greatest difference in preservation most likely comes from the hotter temperatures and heavier rainfall at FARF.

Current studies on residue preservation and diagenesis are relatively few and have often been conducted under field conditions (Cnuts et al. 2017; Langejans 2010; Monnier and May 2019). Future research should be conducted in a laboratory setting focusing on isolated variables, such as pH level, UV exposure, or freeze-thaw cycles, (e.g. Braadbaart et al. 2009) to reach a better understanding of how specific burial conditions and environmental factors affect different adhesive types. Additionally, by exposing experimental residues to artificial accelerated ageing conditions, archaeologists will be able to gain a more accurate understanding of the decomposition curves of these materials.

Archaeological comparisons

Despite only being in the ground for 2 and 3 years, the preservation indices assigned to the adhesives studied here match our predictions and align well with what is known from the archaeological record. The oldest known archaeological adhesives are birch bark tar (Mazza et al. 2006), which are approximately 150,000 years older than the oldest resin adhesives (Charrié-Duhaut et al. 2013; Degano et al. 2019). Results here show that birch bark tar preserves considerably better than any other adhesive tested, so it is not surprising that the oldest known adhesives are of this material. Birch tar is a highly suitable material to haft stone tools with and may have been preferred because of its reusability, workability, and cohesive strength. Birch tar also has known antibacterial properties (Yogeeswari and Sriram 2005) and is more able to withstand both high- and low-frequency forces at a range of different temperatures (Kozowyk and Poulis 2019). These properties support the high preservation index of birch bark tar. However, there are specific circumstances where a strong adhesive is not necessary, such as for hunting implements that are intended to dislodge in their prey (Wadley et al. 2015). Adhesives such as pine resin were also likely obtained more easily than investing in producing birch bark tar. Resin adhesives may well have been employed as early as birch bark tar, but simply does not preserve as well.

The adhesives with the second highest preservation index are also what we find archaeologically from the Middle Palaeolithic and Middle Stone Age; only these are found considerably later than the oldest known birch bark tar (Charrié-Duhaut et al. 2013; Degano et al. 2019). These include compound adhesives of resin, beeswax, and ochre. A mixture of all three of these ingredients was the strongest potential resin-based adhesive according to an earlier study (Kozowyk et al. 2016), so it most likely resists physical decay better than resin or beeswax do individually.

Resin-based adhesives have also been identified from the Middle Stone Age but may be under-represented compared with compound adhesives because of preservation and identification biases. For example, discolouration of a residue may lead to misidentification (cf. cf. Baales et al. 2017). The presence of iron oxide also significantly improves visibility of residues. However, ochre does not necessarily indicate the presence of a hafting adhesive, as it can also be used for aesthetic or symbolic reasons. Decayed resin and tar adhesives can sometimes appear visually similar to sediment, or to mineral deposits, especially when only in trace amounts (Croft et al. 2018). Traces of manganese, for example, frequently occur in sediment and can closely resemble small specks of tar. Adhesives can also be mixed with sand, soil, or clay, as a

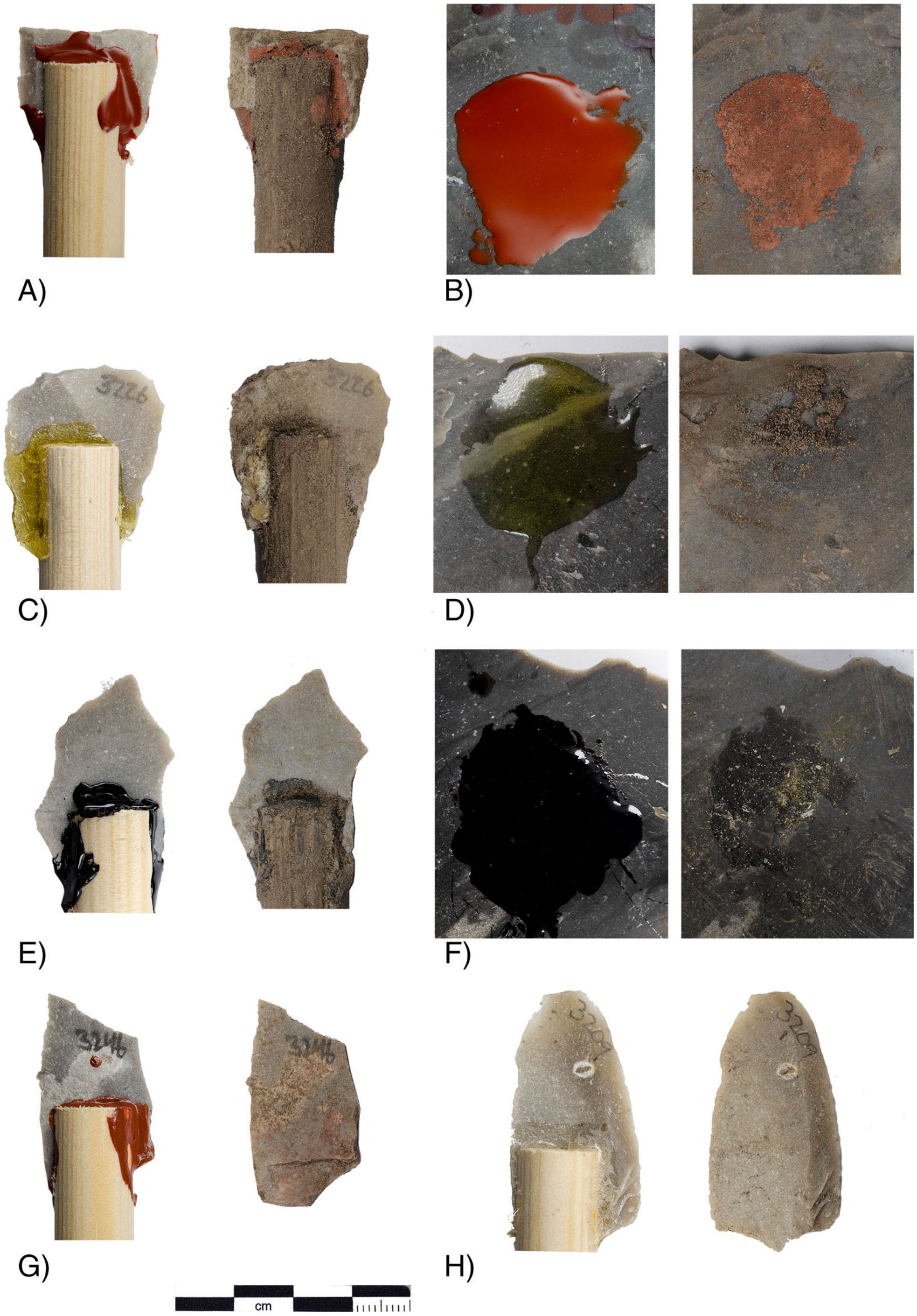


Fig. 8 Before (left) and after (right) photos of birch tar (a, b); resin (c, d); and resin/beeswax/ochre (e, f) hafted and non-hafted flakes; and gum/ochre hafted flakes (g, h) at Horsterwold for 3 years

filler (Dickson 1981; Rots 2008), thus making the visual identification of trace residues even more difficult. However, the presence of red ochre on lithics makes residues more visible.

Pine tar was used extensively in historic times, but its use in the Palaeolithic is less clear. The disparity between birch bark tar and pine wood tar during the Palaeolithic is unlikely to be caused by environmental or resource constraints, as birch and pine occur together throughout much of the Pleistocene in Europe (Bigga et al. 2015). During the Iron Age, birch bark was also utilized specifically to make tar in an environment where pine was more common (Rageot et al. 2016). The use of birch bark tar and its survival in the archaeological record must therefore be due to technological or taphonomic reasons. Birch bark has been proven to be a very suitable material for producing tar by relatively simple processes (Kozowyk et al. 2017b; Schmidt et al. 2019). Whether pine tar can also be produced by similar methods is to be tested. Yields in our experimental production here (using a laboratory kiln) were considerably higher for birch bark than for pine wood, which suggests birch bark is a better candidate for producing tar on a small scale. However, wood that is highly rich in resin content (fatwood) might significantly increase the yield efficiency of pine, although harvesting fatwood might be more exhaustive than collecting birch bark. One explanation for the absence of pine tar during the Palaeolithic, and even for the predominant use of birch tar during the Neolithic (Regert 2004), is that pine tar does not preserve as well as birch bark tar. The clearest example of this is with the non-hafted flakes from Horsterwold—birch tar appeared as new, even after 3 years, and pine tar was almost entirely removed, leaving only small fragments and some discolouration of the flint.

From the Late Middle Stone Age in southern Africa, there exist several sites where hafting adhesives have been inferred from the presence of ochre residues. Experiments here show that when ochre-loaded adhesives (in this case acacia gum) degrade, they often leave a visible ochre staining. A similar pattern might also form given enough time with the resin/beeswax/ochre adhesives. However, there are two issues are of concern here: (1) if the adhesive was loaded with clay or a mixture with lower concentrations of iron oxide, instead of bright red ochre, the visual identification of hafting residues would be easily overlooked. (2) As was shown with some of the experimental samples here, the adhesive residue after recovery is not always present in the same position as when it was originally applied. If the presence of ochre residue is to be used to infer hafting based on its location, then it should be considered that the residues are not all in their original position.

Lombard (2007) showed that micro-residues on tools made from quartz had fewer ochre residues than tools made of hornfels and dolerite. She suggests that this may be the result of a known choice to apply different adhesive recipes for different hafting requirements. However, it is also mentioned that during replication (Lombard and Wadley 2007), residues do not adhere to quartz to the same degree as other course and more porous materials. Differential preservation on various lithic raw materials or in different environments might also explain these differences. Preservation is clearly something that needs to be considered in these situations. More controlled experiments testing the same residues on different lithic raw materials would provide useful information.

The preservation of gum adhesives without ochre, and of hide or bone glue in the archaeological record, is exceptionally rare. Under extremely dry conditions, or waterlogged sites, hide glue may preserve for long periods of time. For example, the oldest animal glues in Europe come from a waterlogged site in Switzerland dated by dendrochronology of the bow wood they used on to a little over 3100 B.C. (Bleicher et al. 2015), and the oldest known animal-based glue currently come from a cave site in Israel and date to between ca. 8200 and 7300 cal. BC (Solazzo et al. 2016). Both sites used in this study, Horsterwold and FARF, receive a considerable amount of precipitation, but are not waterlogged.

Acacia and other plant gums are polysaccharides with high water solubility and low viscosity (Daoub et al. 2016). Until recently, no plant gums have been identified from prehistory. This is likely due to their poor preservation as most plant polysaccharides are rapidly decomposed in soil, sometimes within 6–8 weeks (Martin 1971). However, the FTIR analysis from Grotta del Cavallo, Italy, suggests that Uluzzian backed pieces may have been hafted with a mixture of gum, ochre, and beeswax (Sano et al. 2019). Unfortunately, many of the spectral peaks used to identify gum by the authors also occur in other materials. Polysaccharides also make up 75% of the dry weight of plants (Tseng 1997), further complicating the accurate identification of gum residues. A combination of beeswax and ochre may help inhibit the biological decay of gum adhesives. More specific experiments would need to be conducted to explore this particular combination. If the identification by Sano et al. is correct, however, it highlights the importance of chemically analysing hafting residues, because organic material may be embedded in inorganic remains, even if not microscopically visible. Indeed, there are numerous examples highlighting the visual ambiguity of many micro-residues (Croft et al. 2016; Monnier et al. 2012, 2013; Pedergnana et al. 2016). That the visual identification of the three types of known adhesive residues in this study (gum, hide, and bone glue) was impossible after just 6 months of natural exposure further supports this.

In addition to birch bark tar being the oldest known archaeological adhesive, residues of this material also survive in the largest pieces. Whether this has more to do with how much of the material was initially used is unknown, but samples from Campitello Quarry, Italy, and Zandmotor, the Netherlands, both have tar likely covering more than 30% of the tool's surface area. In the case of Campitello Quarry, this is an estimate, because the exact size of the flake under the tar is unknown. The second object from Campitello Quarry has approximately 25% of one side covered in birch bark tar. The tar from Konigsaue, Germany, although no tool is available for reference, preserved so well that a fingerprint is visible on its surface, suggesting very little, if any, degradation occurred (Koller et al. 2001). Measurements from backed pieces where macro-residues survive from Diepkloof Rock Shelter, South Africa, show that the resin adhesives covered on average approximately 28% of the tool surfaces (Fig. 2 1-5; Charrié-Duhaut et al. 2013). Tools from Fossellone Cave, Italy, show that the resin and beeswax residue covered approximately 23% of the tool surface, while two tools with resin only averaged residue on approximately 5% of the tool surface (Fig. 2A, D, E; Degano et al. 2019). Though these measurements must be interpreted with caution as they are taken from selected figures in the literature that showed clearly the residue and both sides of the tools, we do not know how much of the tools were originally covered by adhesive. However, they give an indication as to how little adhesive residues may degrade under certain circumstances. Birch bark tar and some resin and resin/beeswax adhesives appear fairly similar after 3 years as they do after 50,000 years. That some adhesives were significantly affected after only 6 months to 3 years, both buried and on the surface, also suggests that if decay is going to happen, it may occur relatively quickly after deposition, regardless of rapid burial by sediment (cf. Barton 2009).

Conclusion

Adhesives provide a unique window onto past technologies and human behaviour. The selection and use of different hafting materials may be the result of environmental constraints, production complexity, physical or material properties, the intended function, or possibly even sociocultural or economic factors (Berdan et al. 2009; Kozowyk and Poulis 2019; Kozowyk et al. 2017b; Wadley et al. 2004). It is the variation in adhesive properties that can give so much information about the past that also directly affects how likely the materials are to survive to be analysed by archaeologists in the first place.

The research presented here provides a first look at the preservation qualities of natural adhesives and how this affects the archaeological record. The findings clearly show that birch bark tar preserves better than any other adhesive material tested. Compound resin/beeswax/ochre adhesives preserve more consistently than most others, although the error ranges overlap at the 95% confidence interval. Resin/beeswax, resin, and pine tar adhesives preserve equally well as one another. Ochre also greatly aids in the recognition of potential hafting residues due to its colour.

Archaeologists' understanding of Palaeolithic adhesive use is changing rapidly. We now know that Neandertals chose to invest considerable amounts of birch bark tar to use on small and simple flakes (Niekus et al. 2019). Previously, these types of lithics would not warrant residue analysis, unless as a random control sample to test against such 'likely' hafted pieces as backed bladelets, microliths, or possible projectile points. We also know that as well as birch bark tar, Neandertals were using bitumen, resin, and possibly beeswax (Boëda et al. 2008b; Degano et al. 2019). Adhesives by southern African humans are equally as diverse, but none are as old as the bitumen or birch bark tar finds. Adhesive technology in the deep past was likely more varied than we currently have evidence for. It is important to remain open to the possibility that a wider variety of adhesive types will be found on even more types of stone tools and flakes and, finally, to remember that the life of an adhesive does not end after it is discarded. It remains fluid and can migrate across surfaces, change colour, or disappear entirely.

Acknowledgements We thank Hayley Mickleburgh for transporting, placing, and collecting all of the FARF samples over the 2 years that those experiments took place and Sylvia Rose, Morag Orchard, Tom Withycombe, and Diana Murphy for their supply of birch bark. We would also like to thank Rebecca van der Ham, Leiden University, for assisting with the pH analysis of soil samples.

Funding information This research was funded by an NWO Veni Grant (grant holder: G.H.J.L.), project title: 'What's in a plant? Tracking early human behaviour through plant processing and exploitation' (grant number 275-60-007), and an Archon PhD grant (grant holder P.R.B.K) project title: 'Sticking around: Identification, performance, and preservation of Palaeolithic adhesives' (grant number 022-005-016).

Data availability Not applicable.

Compliance with ethical standards

Conflict of interest The authors certify that they have no affiliations with or involvement in any organization or entity with any financial or non-financial interest in the subject matter or materials discussed in this manuscript.

Code availability Not applicable.

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