Thermochimica Acta 498 (2010) 106–111

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Thermal transitions in high oil content petroleum-based wax blends used in granular sport surfaces

J.W. Bridge[a,*], M.L. Peterson[a], D.W. Radford[b], C.W. McIlwraith[c]

[a] *Department of Mechanical Engineering, University of Maine, Orono 04469, United States*
[b] *Department of Mechanical Engineering, Colorado State University, Fort Collins 80523, United States*
[c] *Gail Holmes Equine Orthopaedic Research Center, Department of Clinical Sciences, Colorado State University, Fort Collins, 80523, United States*

ARTICLE INFO

Article history:
Received 18 May 2009
Received in revised form
29 September 2009
Accepted 11 October 2009
Available online 20 October 2009

Keywords:
Paraffin wax
Microcrystalline wax
Differential scanning calorimetry (DSC)
Gas chromatography (GC)
Paraffinic oils
Synthetic horse tracks

ABSTRACT

Five waxes were extracted from five different synthetic horse race tracks in the United States. These tracks included two cool weather tracks (Kentucky and Northern California) and three warm weather tracks (Southern California). All of these tracks operate over a significant range of temperatures and some even have large temperature swings within a single day of operation. Waxes used in these surfaces are generally a blend of normal paraffins, hydrocarbon oil, and microcrystalline wax that most likely originated from a de-oiling process where the lower carbon distributions had been removed. In this work, a solvent separation was used to remove the wax from samples of material obtained from each of these five tracks after they had been used for at least 3 months. The drop melt temperatures of the wax separated from the five tracks ranged from 67 to over 84 °C. Gas chromatography (GC) tests showed *n*-paraffin mass percentages ranging from 31.4% to 37.9% with the more complex oil and microcrystalline isomers making up the remainder. The drop melt temperatures increased as the ratio of weight average molecular weights for normals and isomers for each wax approached one. GC carbon distributions spanned from approximately C22 to C67. Curves for waxes obtained using differential scanning calorimetry (DSC) for each wax also showed distinct thermal behavior. All of the waxes show indications of two thermal peaks; however, in several cases the peaks showed significant overlap. Two wax samples also had small tertiary peaks. One wax contains two well-defined GC distributions of *n*-paraffins (low and high number carbon) and isomers and is believed to be a blend of two different waxes. The first peak corresponds to paraffin wax melting temperature ranges while the secondary and tertiary peaks correspond to melting of high carbon number microcrystalline wax and other complex isomers containing high melting temperatures. The DSC melting transition temperatures for all the waxes studied were found to occur within expected operational temperature ranges for racing surfaces. The temperature range was obtained from a representative track over a 4-day period of operation. Given the observed changes in the properties of the waxes it is possible that the mechanical properties of the tracks will also change with temperature. The results from this analysis suggest important temperatures to consider for further analysis of the materials containing these high oil content waxes.

1. Introduction

Horseracing is an important industry in the United States and in many countries around the world. In 2004 the American Horse Council funded a study which was performed by Deloitte Consulting [1]. This study estimates the economic impact of horse racing on the United States economy to be at least 26.1 billion dollars. Within the context of this large industry the economic cost of catastrophic injuries to race horses is a significant factor. Catastrophic injuries include injuries that significantly alter the ability of the horse to continue to race or result in loss of the animal. A study in the 1980s by the American Association of Equine Practitioners estimated that annual loss of horses is on the order of $500 million [2,3].

The California Horse Racing Board declared that all major tracks in the state must install a synthetic track surface by the end of 2007. This rule was motivated by testimony that indicated that these surfaces were significantly safer than traditional dirt racing surfaces [4]. In general, this has been born out with a significant reduction in catastrophic injury at some tracks. For example, one racetrack showed 75% reduction in catastrophic injuries during racing from the last year of the dirt track 2006, to 2007 the first year of racing on the synthetic racing surface [5].

Concerns also exist with the synthetic tracks. These surfaces have been noted for being slow in several cases [6] and fast in oth-

---

[*] Corresponding author. Tel.: +1 207 326 2376; fax: +1 207 326 2510.
E-mail address: john.bridge@mma.edu (J.W. Bridge).

0040-6031/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2009.10.009

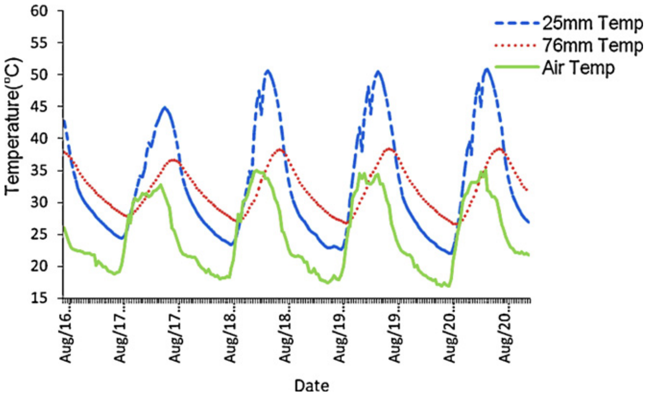

Fig. 1. Del Mar synthetic track temperature profile over 4-day race period (August 16–20, 2007).

ers [7]. One synthetic track in 2007 had an average 6 furlong race time that was 1.9 s slower than the average 6 furlong race time on the dirt track in 2006 [8]. There is a clear perception that the speed of the synthetic tracks also tend to vary with temperature [5]. The temperature range experienced by these surfaces in operation is quite large. Fig. 1 shows the temperatures measured on one synthetic track surface (Del Mar, California) over a 4-day period in 2007. Track temperature fluctuations of over 30 °C are seen in the course of a single day.

The question which will be considered in this work is whether these temperatures correspond to any significant changes in the track materials. The composition of these tracks suggests a likely source of variation. The synthetic tracks are made of relatively thermally stable components including polypropylene fibers, rubber, and silica sand. However all of these components are given a wax coating. Fig. 2 shows a photograph of one of the track samples used in this study. The wax used in most of these surfaces is a slack wax which is sometimes mixed with more highly refined paraffin and microcrystalline waxes. The slack wax originates from the bottoms of distillation columns during the petroleum oil refining process and consists of primarily linear *n*-paraffins containing 18–40 carbon atoms (C18–C40), hydrocarbon oil, and a small percentage of branched isoparaffins and cyclic alkanes (naphthenes) [9]. The oil content can range from 3% to 50% depending on the crude oil from which it is derived and to the extent to which the oils present are separated [10]. Both paraffinic and naphthenic oils may be present. Microcrystalline wax (C25–C85) added to paraffin wax–oil blends can help to help stabilize the oil content [11] and to optimize properties such as melting point and viscosity. Microcrystalline wax additions are also known to improve cold temperature flexibility of paraffin wax [12]. The oils and microcrystalline waxes both contain more complex molecular structures that may include higher percentages of branched paraffins, cyclic alkanes, and substituted aromatics [13].

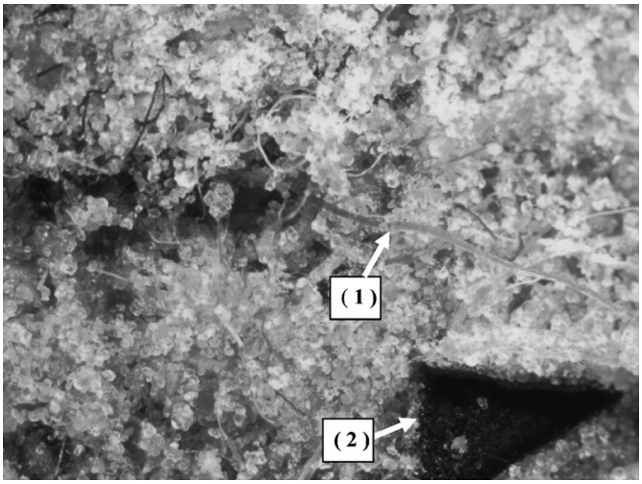

Fig. 2. Photo of Keeneland synthetic wax-coated track material (14×). Silica sand particles are mixed with wax, polypropylene fibers (1), other organic fibers and rubber particles (2).

Previous literature on the type of wax used in these tracks is limited. In most other applications oil is usually removed (to less than a few percent) prior to use. Therefore the properties of waxes with high oil contents are less well understood. In order to determine the effects of wax on the track performance, it is necessary to both measure the properties of the waxes and to better characterize the waxes used in this application. Five representative synthetic horseracing surfaces are considered. Because of the requirement that synthetic tracks be installed in California, four California tracks were included. Material was used from Hollywood Park in Inglewood California, Golden Gate Fields in Albany, CA; Del Mar in Del Mar, CA; Santa Anita in Arcadia, CA and Keeneland in Lexington, KY. Keeneland was included to represent a surface used in a more variable climate and because it uses a wax-coated recycled material as one of the components. These five racetracks represent typical operating conditions for North American racing. The more arid and higher temperatures experienced by tracks in Southern California are in contrast to the greater rainfall and cooler climate of Golden Gate Park. The track at Keeneland is used year around and includes usage during cold winter and hot summer periods. All tracks with the exception of Del Mar are used for training year around.

In order to understand the composition and thermal response of the wax, density measurements, drop melt temperature tests, differential scanning calorimetry and gas chromatography were used. An *n*-octadecane paraffin wax was utilized as a control sample. The outcome of this testing will result in a better understanding of the temperature ranges which should be considered for testing of the track surfaces.

2. Experimental

2.1. Materials

Synthetic track samples were taken from five tracks after they had been in use for at least 3 months. Sampling of the track material was performed using a soil-sampling probe to remove a cylindrical section of the track surface to a depth of approximately 3 in. The tracks are designated in the results by the notations; Del Mar (DM), Santa Anita (SA), Keeneland (KL), Hollywood Park (HW), and Golden Gate Fields (GG). These samples of track material represent three major vendors of synthetic tracks; Polytrack (DM, KL), Cushion Track (SA, HW), and Tapeta Footings (GG). The slack wax used in these tracks has a high oil content approaching 20% and higher. Microcrystalline wax is also present and is estimated between 5% and 50%. The Keeneland track material differs from the other samples in that it contains a recycled component referred to as “jelly cable”. The jelly cable includes both a polymer wire casing material and the wax coating used to facilitate pulling the cable though the housing. The wax coating from the recycled jelly cable would represent one component of the separated wax for this sample.

The waxes were extracted by using a high-purity iso-octane solvent extraction applied to the track material. The solvent (250 ml) was mixed with 300 g of each track material (2 replicates per sample) in a 500 ml glass beaker and placed in an ultrasonic bath for 2 h; after which, the solvent with dissolved wax was decanted into a second beaker. This beaker containing solvent and dissolved wax

Table 1
Physical description of separated wax samples.

Wax sample	Density (g/cc)	Color	Relative opaqueness	Percent wax mass (%)
n-Octadecane[a]	0.770	White	1	NA (control)
GG	0.785	Golden-brown	2	5.9
SA	0.862	Golden-beige	2	5.5
HW	0.764	Dark brown/green	3	5.3
DM	0.767	Brown	3	5.0
KL	0.807	Brown-black	3	7.3

[a] Note the *n*-octadecane control sample is hard/brittle in texture versus the others that are very soft in comparison.

was then placed into a furnace set to 100 °C to evaporate the solvent. Fresh solvent was then poured into the material beaker and the process repeated two more times. After the third decanting and furnace evaporation of solvent from both beakers, the beakers with contents were weighed and compared to the initial weights and percent wax was calculated. A detailed description of this procedure can be found online [14].

The texture and visual appearance of these waxes ranged from soft to soft/firm with varying density, opacity and color. The degree of opacity of wax/oil blends and color may give a qualitative indication of oil content for future samples once chemical analyses have been catalogued and baselines are established for various waxes. Increased softness accompanies an increase in oil content as demonstrated by needle penetration tests. Kumar et al. [12] showed needle penetration values of 21 dmm for a wax–20 wt% oil blend versus 9 dmm for wax–14.6 wt% oil (50 g, 5 s, 30 °C). The samples for this study were similar in softness and densities with degree of opacity ranked as shown in Table 1 above (“3” being the most opaque). The mass percent of wax extracted is also given.

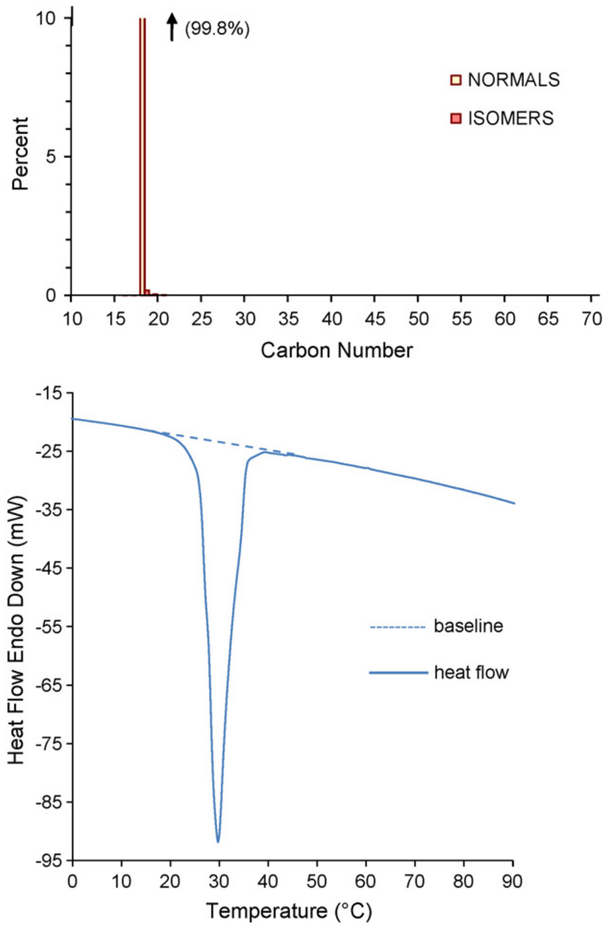

Fig. 3. GC distribution (upper scan) and DSC melting endotherm (lower scan) for *n*-octadecane wax control sample. (*Note:* the DSC vertical scale is much larger than other wax scans.)

2.2. Gas chromatography (GC)

Gas chromatography analyses of the samples were performed based on ASTM D5442 [15] using a Hewlett Packard 5890 Series II Gas Chromatograph with flame ionization detector. Hydrogen was used as the carrier gas. The column used was a J&W Scientific capillary column DB-1HT, 30 m, with 0.32 mm inner diameter and 0.1 μm film thickness. Detector gasses employed were hydrogen at 30 ml/min and air at 400–450 ml/min.

2.3. Drop melt tests

Drop melt tests were conducted based on the standard test developed to determine the wax melting temperature (ASTM D127) [16]. Each sample was melted to approximately 6–11 °C above its drop melt temperature and chilled thermometer bulbs were immersed into the samples and withdrawn. Two samples of each wax sample were prepared, placed into corked test tubes and inserted into water baths with controlled heating. Drop melt tem-

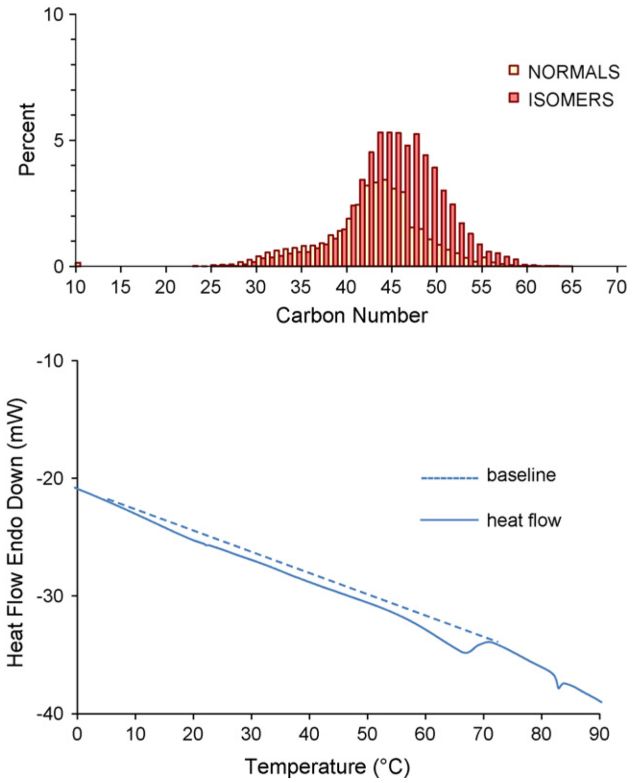

Fig. 4. GC distribution (upper scan) and DSC melting endotherm (lower scan) for Hollywood Park track wax sample.

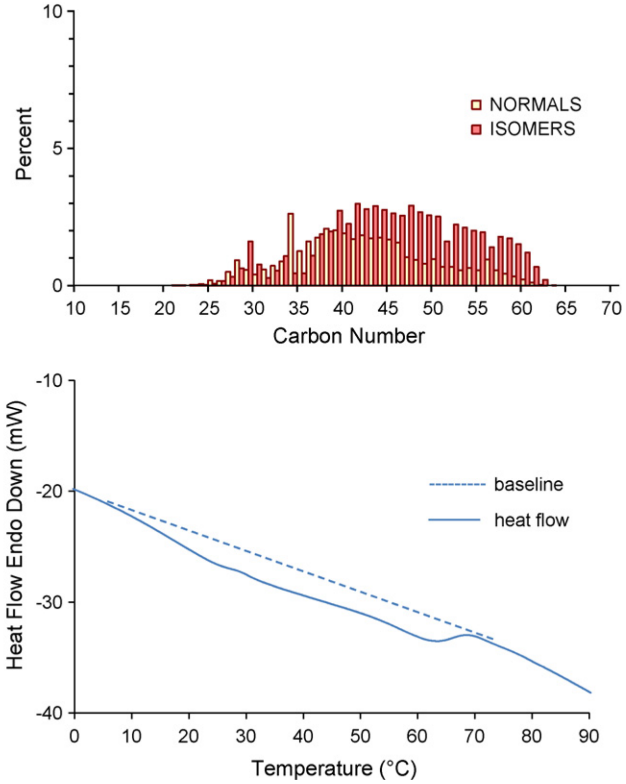

Fig. 5. GC distribution (upper scan) and DSC melting endotherm (lower scan) for Golden Gate Fields track wax sample.

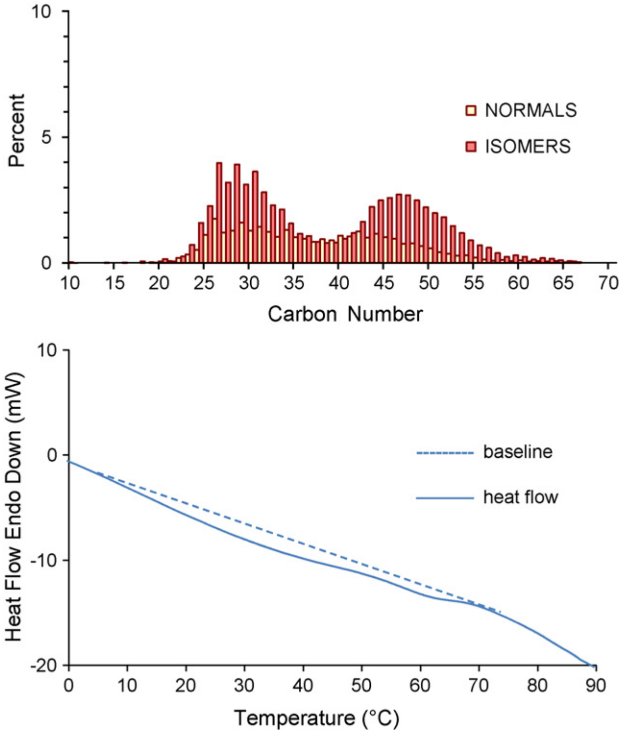

Fig. 6. GC distribution (upper scan) and DSC melting endotherm (lower scan) for Keeneland track wax sample.

peratures were reported as the average value of each pair of samples.

2.4. Differential scanning calorimetry (DSC)

Differential scanning calorimetry was performed in a PerkinElmer Pyris1 with power compensation under nitrogen flow (20 ml/min). Two samples (9–11 mg weighed to 0.1 mg precision) of each wax were prepared in aluminum sample pans and heated from 20 to 93.3 °C, 93.3 to −30 °C, then −30 to 93.3 °C. The thermal sequence of the tests used was consistent with the standards for DSC wax testing ASTM D4419 [17]. Transition ranges and melting temperatures were taken from the second heating run and are plotted with endotherms pointing downwards.

3. Results and discussion

Fig. 3 shows GC and DSC data for *n*-octadecane, a linear paraffin wax containing 18 carbon atoms per molecular chain. The control sample has a very well-defined solid-to-liquid transition peak and high melting enthalpy characteristic of a crystalline paraffin wax. In contrast, Figs. 4–8 show the GC and DSC curves for the wax blends which show extended solid-to-liquid temperature transitions and much lower melting enthalpies. The wax blends contain a much higher range of molecular mass fractions and oil content which leads to less prominent, wider endotherms. The linear-chained molecules (bars) depicted on the GCs are referred to as “NORMALS” versus the more complex molecular chains or “ISOMERS”. The GC and DSC curves for each specimen are displayed together to highlight correlations between structure and thermal behavior.

The GC data suggests that the extracted waxes are formulated waxes that result from further refining or “de-oiling” processes where the lower carbon number paraffin chains have been removed (up to approximately C32) [18] leaving higher carbon number distributions (C32–C67) and higher percentage of oil. It is difficult to pinpoint the exact amount of oil present using GC since isomers may contain both solids and oils, though the soft consistency of all

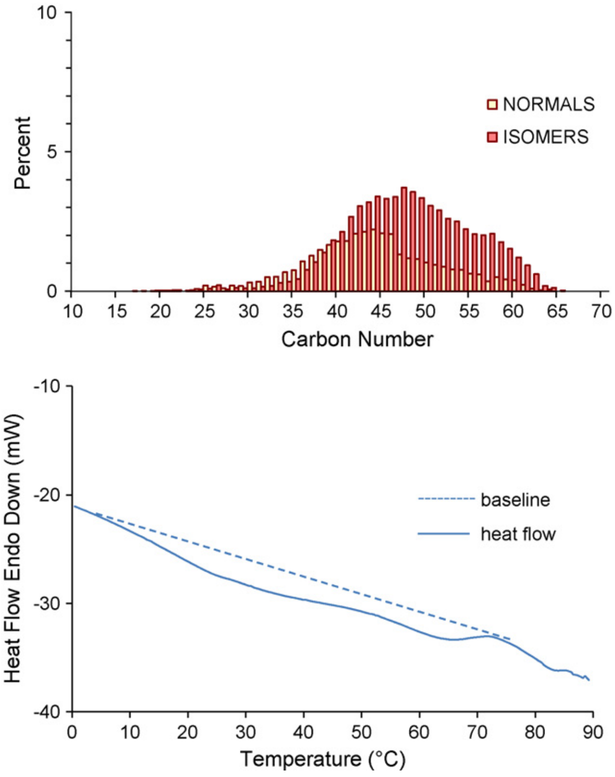

Fig. 7. GC distribution (upper scan) and DSC melting endotherm (lower scan) for Del Mar track wax sample.

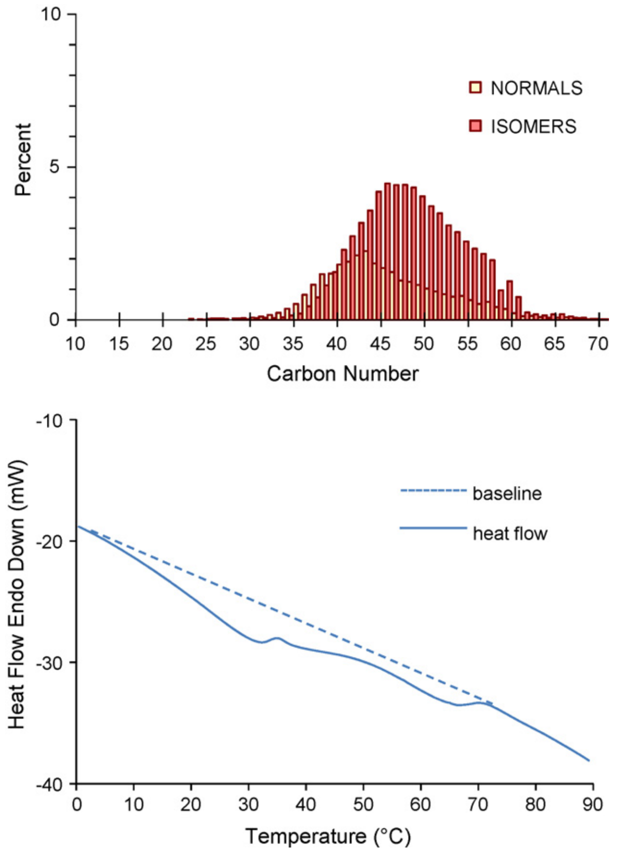

Fig. 8. GC distribution (upper scan) and DSC melting endotherm (lower scan) for Santa Anita track wax sample.

the blends, and *n*-paraffin percentages ranging from 31.4% to 37.9%, suggest significant oil content remaining in all of the wax blends. The less Gaussian shapes of the isomer distributions for the GG, DM and SA waxes also suggest that there is a higher percentage of microcrystalline wax present in these blends, though all the blends show low quantities of carbon distributions beyond C60 which can signify microcrystalline wax. The GG wax, in particular, strongly resembles a microcrystalline slack wax [10].

Note that all the blends show from very slight (HW) to more pronounced (SA) indications of a first DSC thermal transition peak that correlates directly to the corresponding GC carbon *n*-paraffin distribution. With the exception of HW that showed a slight first peak transition at 22 °C, the other four waxes showed this peak at between 31 and 33 °C. All waxes showed the second DSC transition peak at between 63 and 65 °C, which corresponds to the higher carbon number distributions and associated melting temperature range for microcrystalline wax (54–95 °C). High melting point microcrystalline wax additions or complex isomers such as those from black tar distillation bottoms containing asphaltenes may also be the reason that both HW and DM show distinctive, isolated tertiary peaks at 83 °C (note the small amount of higher carbon isomers present in GC scan for both HW and DM at C65). For the KL wax, it appears that a second paraffin blend with lower number carbon chains was added to the wax to replenish the lower carbon *n*-paraffins that were originally removed. The result is a unique *n*-paraffin/isomer distribution with double broad peaks and significantly increased carbon number distributions between C22 and C35.

Table 2 summarizes the properties of these waxes taken from density measurements, drop melt tests, and information from GC/DSC tests. The total melting enthalpy is the average of two test runs for each sample. The samples are ordered by increasing *n*-paraffin percent. There is a direct correlation between *n*-paraffin content and sample density with density decreasing as *n*-paraffins increase. This is expected due to the lower molecular weight of *n*-paraffins versus the more complex isomers (the higher GG density may be attributed to experimental error). It has also been shown in petroleum wax composition/expansion studies [19] that for very long *n*-paraffin and isoparaffin chains, there can be a depressing effect on expansion with temperature after a certain chain length due to greater twisting and curling of chains (thus impeding closer packing). In our study, as the isomer percentage increases, there may be a predominance of moderate sized isomers, simple isoparaffins (with limited/short side chains), and ring structures that lead to more efficient localized packing of atoms within the molecules contributing to higher density. There also seems to be a correlation between drop melt temperature and mass percent isomers present with a general increase in drop melt temperatures as the percentage of isomer increases. Note that the Keeneland wax drop melt temperature is higher than what is reported—the water bath came to a boil before a wax drop separated from either sample bulb. There is also a direct correlation between drop melt temperatures and the ratio of normal to isomer weight average molecular weights for each wax. As this ratio approaches one (equal weights of each), the drop melt temperatures increase accordingly. The melting enthalpies generally track with size of the transition region, though higher oil content has a diminutive effect on melting enthalpy as does an increase in complex hydrocarbons/molecular weight [9,20]. The gradual DSC initial transition onset slopes characteristic of all the waxes may be indicative of the influence of naphthenic oils that show an increasing slope as the heat capacity changes [21]. The double peaks associated with the KL wax provide for increased lower-end carbon number distributions versus the other waxes, but overall, it contains the second lowest total

Table 2
Wax properties.

Wax	*n*-Paraffin (%)	Isomers (%)	Density (g/cc)	M_w *n*-paraffin (g/mol)	M_w Isomers (g/mol)	Drop melt (°C)	Primary/secondary melting range (°C)			Tertiary melting range (°C)		Total avg. melting ΔH (J/g)
							Onset	Final	ΔT	Initial	Final	
SA	31.4	68.6	0.86	633	674	77.3	4	71	67	–	–	48
KL	32.0	68.0	0.81	521	536	>84[a]	2	67	65	–	–	36
DM	35.1	64.9	0.77	616	670	75.9	−2	73	75	77	85	54
HW	36.8	63.2	0.76	597	633	77.3	4	70	66	82	84	31
GG	37.9	62.1	0.79	584	642	67.1	7	68	61	–	–	49
n-Octadecane (control)	99.8	0.2	0.76	254	257	28–30[b]	27	36	9	–	–	225

[a] The Keeneland wax samples did not drop before water solution came to a boil. The samples did drop at approximately 95 °C after remaining at a constant water bath temperature for several minutes.

[b] Melting point from Handbook of Chemistry and Physics [22].

n-paraffin content. The high percentage of isomers and close molecular weight distributions most likely contribute to its low melting enthalpy and high drop melt temperature. The higher drop melt temperature also suggests a lower percentage of oil as compared to the other samples. KL also possesses the lowest end-transition temperature of all the waxes.

When the melting transition regions of these waxes, as determined by DSC (Figs. 4–8), are compared to the 4-day operating temperatures of the Del Mar track (Fig. 1), one sees complete overlap. The Del Mar wax experiences some degree of melting throughout the entire operating temperature range. The temperature at the 25 mm (1 in.) depth spanned from approximately 22 to 52 °C (72–126 °F) with the corresponding DSC melting range spanning from 8.4 to 86 °C (47–187 °F). From Table 2 one can see that all the tracks share similar melting responses, with DM demonstrating the largest melting enthalpy (54 J/g) followed by GG (49 J/g) and SA (48 J/g). The HW and KL tracks showed the lowest melting enthalpies at 31 and 36 J/g, respectively.

4. Conclusions

Gas chromatography and differential scanning calorimetry as well as drop melt tests provide useful information in the characterization of wax–oil blends extracted from horse tracks. All waxes in this study are believed to have originated as the wax–oil remnants from de-oiled slack waxes and have high oil content and *n*-paraffins beginning around C25–C32 and peaking at C40–C47. The Keeneland wax showed a double peak distribution with an initial *n*-paraffin peak at C27 and the second at C43 indicating that it is a blend of two waxes. The solid-to-liquid transition regions for all waxes are very wide due to the different mass fractions in each of the blends with DSC thermal response correlating overall to GC carbon distributions. No two tracks are identical in either carbon number distributions, oil content, or range/size of melting transition regions; though onset and end thermal transition temperatures are similar and carbon peak regions are fairly close. For a typical range of operating temperatures experienced by the Del Mar track, it is readily apparent that the wax is undergoing various degrees of melting. This general response is shared by all the tracks in this study. Future work will involve track material tests at various temperatures to determine if observed differences in thermal wax response are associated with changes in the mechanical properties of the track. This information can either lead to changes in the types of wax used in the track or the development of cooling procedures such as watering of the track to maintain the track within a target temperature range.

Acknowledgements

The authors are grateful to Sean McColl and Steve Bell of International Group Incorporated for gas chromatography support as well as for supplying sample wax. The authors are also grateful to Dr. George Harakkas for his guidance and laboratory support at Maine Maritime Academy, Castine Maine. Partial funding for this research was provided by the Grayson-Jockey Club Research Foundation.

References

[1] American Horse Council Foundation, The Economic Impact of the Horse Industry on the United States, 2005, Washington, DC.
[2] C.W. McIlwraith, Chairman of Blue Ribbon Panel on Racetrack Breakdown, AAEP (1989).
[3] G. Carpenter, in: Race Track Industry Symposium, 11 December 2003, Tucson, AZ.
[4] R. Allison, Thoroughbred Racetracks Installing Synthetic Surfaces, JAVMA News [Online] April 1, 2007, http://www.avma.org/onlnews/javma/apr07/070401o.asp (accessed 15.02.09).
[5] L. Shulman, The Blood Horse 83 (2007) 6975–6982.
[6] Nahill, Slow Classic Raises Questions about Polytrack, North Country Times [Online] August 22, 2007, http://www.nctimes.com/sports/nahill/.
[7] N. Lead, in: Summation Sizzles on Synthetic with Palos Verdes Score, Horse Racing Press Releases [Online], http://www.horseraceinsider.com/blog.php/Press-Release/nite-lead-monday-january-21st-2008/.
[8] Equibase Trackmaster® Downloadable Charts [Online] 2008, http://www.equibase.com/.
[9] J. Stank, J. Mullay, Thermochim. Acta 105 (1986) 9–17.
[10] The International Group Inc., Wax Overview [Online] 2006, www.igiwax.com/resource/Wax_Overview (accessed November 2008).
[11] R.M. Butler, D.M. MacLeod, Can. J. Chem. Eng. 39 (1961) 53.
[12] S. Kumar, K.M. Agrawal, S.P. Nautiyal, Petrol. Sci. Technol. 25 (2007) 1531–1537.
[13] R.C. Barras, J.F. Boyle, C.F. Grainger, Determination of oil in wax by wide line nuclear magnetic resonance, petroleum waxes—characterization, performance and additives, in: Proceedings of ASTM-TAPPI Symposium, 1963, p. 44.
[14] Separation Procedure, Racetrack Surfaces Testing Laboratory [Online] April 5, 2009, http://www.bioappeng.com.
[15] Anonymous, ASTM D5442 Standard Test Method for Analysis of Petroleum Waxes by Gas Chromatography, 2008, American Standards and Testing, West Conshohocken, PA, USA.
[16] Anonymous, ASTM D127 Standard Test Method for Drop Melting Point of Petroleum Wax including Petrolatum, 2008, American Standards and Testing, West Conshohocken, PA, USA.
[17] Anonymous, ASTM D4419 Standard Test Method for Measurement of Transition Temperatures of Petroleum Waxes by Differential Scanning Calorimetry (DSC), 2005, American Standards and Testing, West Conshohocken, PA, USA.
[18] H. Bennet, Commercial Waxes—Natural and Synthetic, Chemical Publishing, New York, 1944.
[19] P.R. Templin, Characterization of petroleum waxes by the behavior of blends with oil or wax, petroleum waxes—characterization, performance and additives, in: Proceedings of ASTM-TAPPI Symposium, 1963, pp. 72–73.
[20] V. Jayalakshmi, V. Selvavathi, M.S. Sekar, B. Sairam, Petrol. Sci. Technol. 17 (1999) 843–856.
[21] C. Giavarini, F. Pochetti, J. Thermal Anal. 5 (1973) 83–94.
[22] Handbook of Chemistry and Physics, 89th ed., CRC, 2009.