Detection and Identification of Waxes, including Punic Wax, by Infra-Red Spectrography
Author(s): Hermann Kühn
Source: *Studies in Conservation*, Vol. 5, No. 2 (May, 1960), pp. 71-81
Published by: Maney Publishing on behalf of the International Institute for Conservation of Historic and Artistic Works
Stable URL: http://www.jstor.org/stable/1504955
Accessed: 13/05/2013 10:20

HERMANN KÜHN

Detection and Identification of Waxes, Including Punic Wax, by Infra-red Spectrography

Received 19/12/59

INTRODUCTION

In ancient times, beeswax was used in many crafts. It was used as an adhesive, as a protective coating on walls and statues, and as a paint vehicle. For the latter purpose, the beeswax was heated with water and soda or potash [1]. The resulting emulsion is generally called Punic wax. In Egypt, it appeared in the Ptolemaic period for painting on wood. Preparations of wax for preserving paintings are said to date back to the XVIII dynasty (*c.* 1500 B.C.) [2].

The chemist in a museum laboratory may sometimes have to detect wax in an object of art. If a big sample is available, wax can be identified by its physical properties. Beeswax melts just above 60° C. (recent species between 60° and 65° C.) without decomposition; liquid wax has a low viscosity; it becomes solid again on cooling; at room temperature it remains plastic.

More often, only very little samples of wax are available, as in the case of the Fayûm mummy portraits, or the thin protective coatings of walls or statues [3], which have been largely rubbed off in the course of time. Furthermore, it is impossible to distinguish beeswax from Punic wax, plant wax, or many synthetic waxes by the above-mentioned physical criteria. A 'classical chemical analysis' of wax is rather difficult and again requires a large sample and much time: waxes are composed of several esters of fatty acids containing a high number of carbon atoms, together with free fatty acids and long-chain hydrocarbons. Only two other methods remain, namely, paper chromatography [4, 5, 6] and infra-red spectrography. We preferred the latter method, because the preparation of samples is easier and so is the evaluation, which involves a comparison of the spectrum of an unknown sample with spectra already known [7, 8].

PREPARATION OF SAMPLES

It is usually impossible to place a small sample of paint-layer directly in the path of the infra-red beam, because of two difficulties. Firstly, the pigment also gives an infra-red absorption spectrum which would be superimposed on the wax spectrum. Besides this, the pigment would scatter a large proportion of the infra-red light, allowing only a weakened beam to pass. Therefore, we first separated pigment and medium. A sample as small as a pin-head was placed on a microscope slide with a recess in the middle, or in a micro-crucible, and chloroform was added. After having been kept for one day at room temperature, the solution was drawn off with a dropper pipette and dropped on a rock-salt plate. The chloroform was then evaporated in a draught of hot air. In this way, we obtained a film of the wax on the surface of our rock-salt plate, which acted as a sample holder.

If wax is mixed with resins such as dammar,

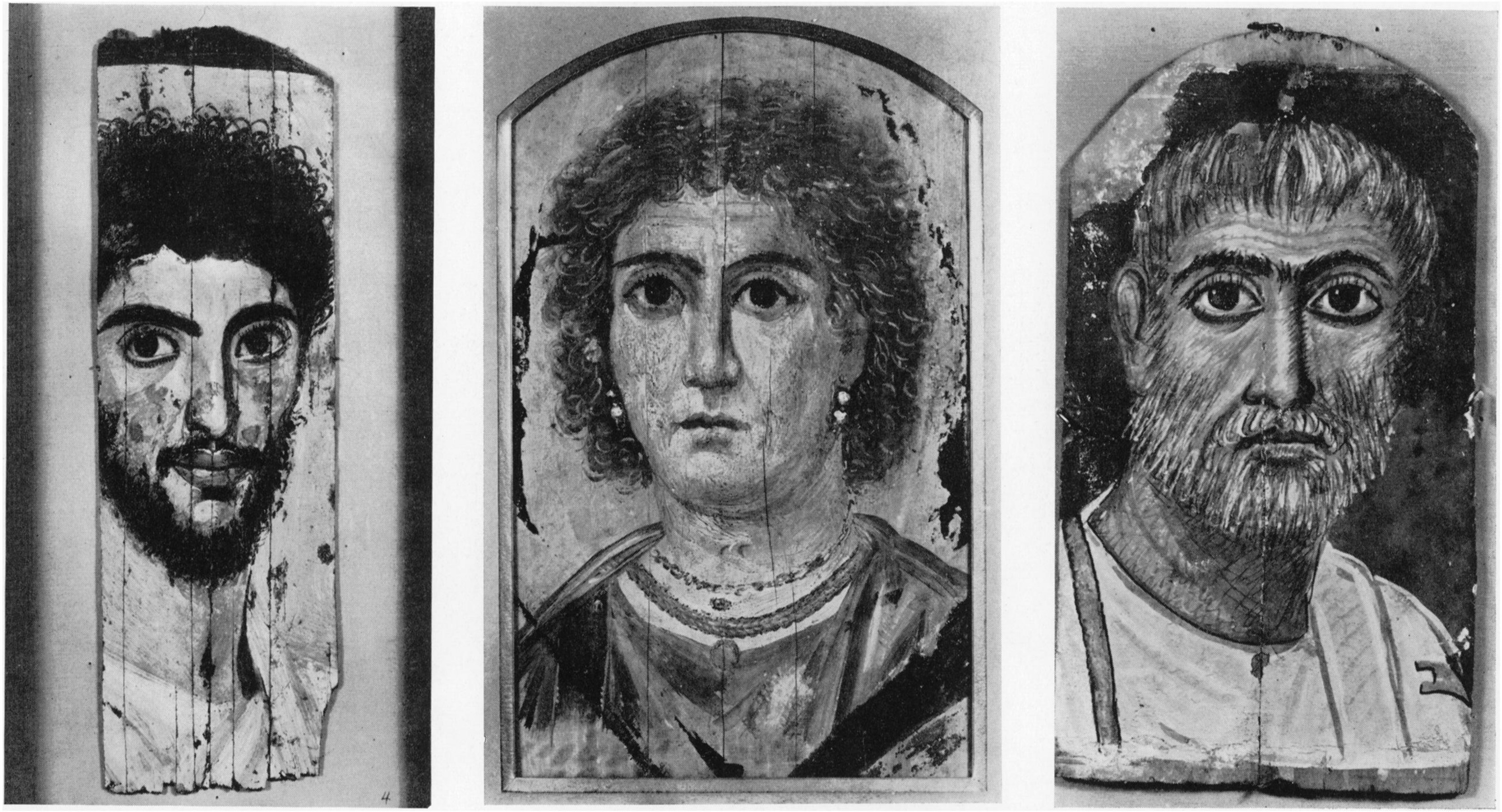

FIG. 1. Three Fayûm portraits. (*Left*) Encaustic on wood, 36 × 11 cm. (*Centre*) Encaustic on wood, 38 × 23 cm. (*Right*) Gum tempera on wood with ground, 26 × 14·5 cm. *Ägyptische Staatssammlung, München, Inv. Nos. 4, 1, and 3.*

mastic, or colophony, it can be extracted with benzyl alcohol, leaving the resin. From asphaltum it can be separated by hot monochlorhydrin ($CH_2OHCHOHCH_2Cl$).

REDUCTION OF SAMPLE SIZE

From paintings or other works of art only milligram or microgram samples may be removed. But in order to get the clearest spectrum the sample must be spread over the whole cross-section of the infra-red beam. For very little samples, the infra-red beam may be concentrated by means of a simple microscope, equipped with rock-salt lenses. This can be supplied by various spectrograph manufacturers. The cross-section of the beam in a Hilger H 800 Recording Infra-red Spectrophotometer can be reduced by such a microscope to 1·3 by 0·2 mm. = 0·0026 $cm.^2$. The extracted paint medium need only cover this small area.

The diagrams published in this paper are run in a Beckman IR 4 spectrograph with microscope, in double beam operation (rock-salt prism). Scanning speed was 0·5 μ/minute, slit-width was controlled automatically (standard), gain was 6·5 per cent., period 2, glower current 0·6 amp.

ANALYSIS OF THE PAINT MEDIUM IN SOME FAYÛM MUMMY PORTRAITS [9]

The extracted media of the paint layers of the portraits shown in Fig. 1 (*left* and *centre*) both gave infra-red spectra corresponding to beeswax (Fig. 2). The spectra were closely similar to those from samples of recent beeswax, and of a wax seal dated 1218. Thus, while oils, resins, and proteins undergo big chemical changes in the course of time, this beeswax has remained almost unchanged for about 1800 years. The portraits are painted directly on wood, without any ground. In mummy portraits belonging to the Louvre beeswax has also been detected [10]. The chloroform extract of another portrait (Fig. 1, *right*) did not contain wax, but a resin, probably shellac. An aqueous extract of the paint layer contained pentoses (indicating plant gums). This portrait has a ground layer between paint and wood. Further examinations of sugars, oils, resins, and proteins by infra-red spectrography are planned and will be reported in detail in another publication.

DIFFERENCE BETWEEN BEESWAX AND PUNIC WAX

Punic wax is beeswax containing salts of fatty acids (soaps). According to a recipe of Pliny [11], beeswax was carefully bleached, and boiled with seawater and some form of soda. By this process, some of the esters and free fatty acids in beeswax, reacting with the soda, would be converted to sodium salts. These salts, generally called soaps, emulsify the unchanged beeswax, allowing it to mix with water to form a paste.

Such wax emulsions may be used as paint media. After drying, there remains a beeswax containing soaps, which give it a melting range extending somewhat higher than pure beeswax. There are a great number of different recipes dealing with the preparation of Punic wax, which is, however, always a mixture of beeswax and soaps.

To demonstrate this, we produced Punic wax in the following way. 100 g. beeswax, 300 ml. water, and 3 g. sodium carbonate were boiled and vigorously stirred; stirring was continued until the mixture had cooled down to room temperature. The creamy emulsion was painted on glass and dried in warm air. The resulting film was transferred by means of an electrically heated spatula to a rock-salt plate. The infra-red spectrum is shown in Fig. 3. The spectrum was that of beeswax with the band at 6·8 μ (1480 $cm.^{-1}$) broadened to the right, and an additional band near 6·35 μ (1570 $cm.^{-1}$). These changes are due to the ionized carboxyl groups of the fatty acid soaps. Ionized carboxyl groups have absorption bands between 6·2 μ (1610 cm^{-1})

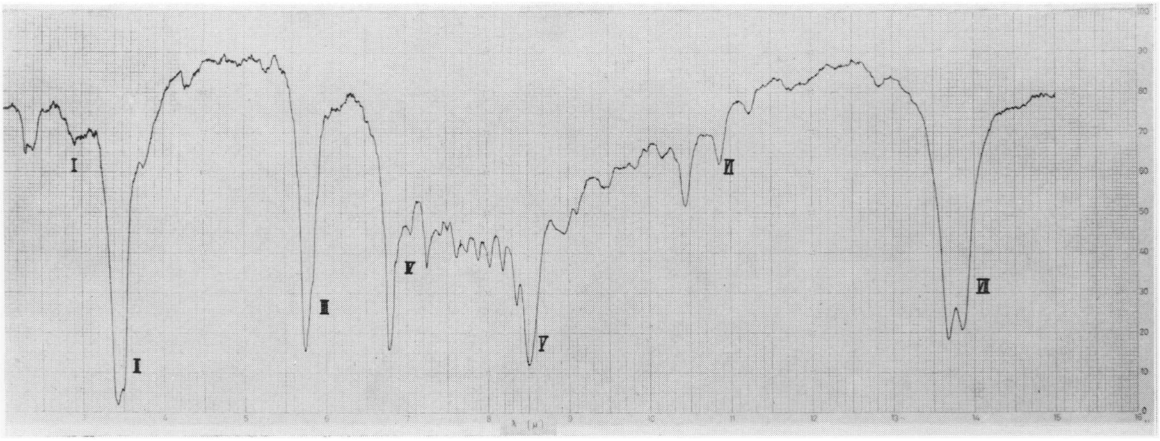

FIG. 2. *Infra-red spectrum of beeswax.* Absorptions numbered I-VII are due to the following chemical characteristics of beeswax: (I) *Hydroxyl-group, OH.* The band at 2.9μ (3450 cm.$^{-1}$) is always present in alcohols. (II) *C-H.* At about 3·4μ (2850 cm.$^{-1}$) lie vibrations common to all compounds with CH, CH_2, and CH_3 groups. (III) *Carbonyl group, CO.* The CO group in esters, present in beeswax, absorbs at 5·75μ (1730 cm.$^{-1}$). The CO group in organic acids (unionized), also present in beeswax, absorbs at 5·85μ (1709 cm.$^{-1}$). Here the ester absorption is much stronger. (IV) *C-H.* 6·8μ (1470 cm.$^{-1}$) and 7·2μ (1388 cm^{-1}). All compounds with band II also have bands IV. (V) *Ester group.* In addition to band III, the esters occurring in waxes also absorb at 8·5μ (1177 cm.$^{-1}$). (VI) *Solid beeswax.* The bands at 10·4μ (962 cm.$^{-1}$), 10·9μ (918 cm.$^{-1}$), 11·25μ (890 cm.$^{-1}$), and also those between 7·5μ (1333 cm.$^{-1}$) and 8·4μ (1190 cm^{-1}) all disappear as soon as beeswax is melted or dissolved. (VIII) *Long-chain hydrocarbons.* Compounds with long chains of CH_2 groups generally have absorption bands at 13·7μ (730 cm.$^{-1}$) and 13·9μ (719 cm.$^{-1}$).

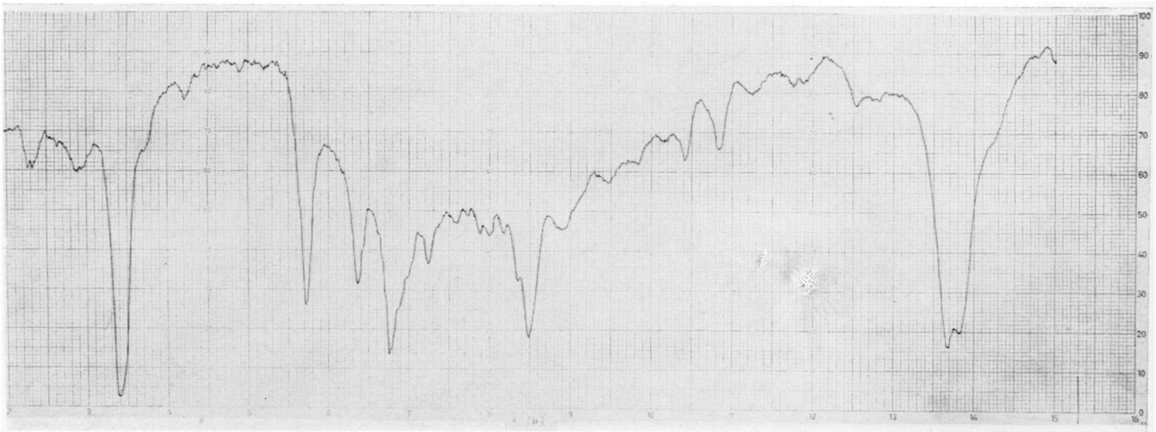

FIG. 3. Punic wax.

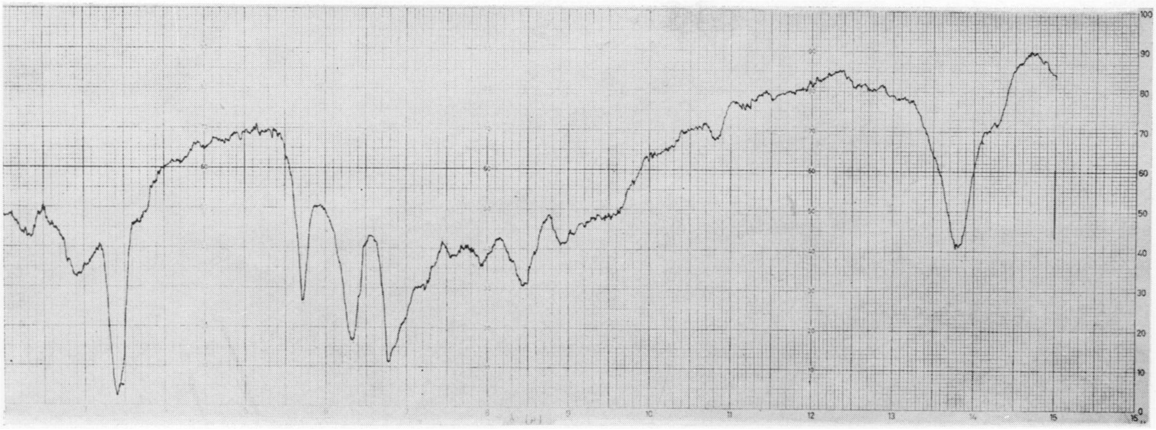

FIG. 4. Alcohol-soluble components of Punic wax.

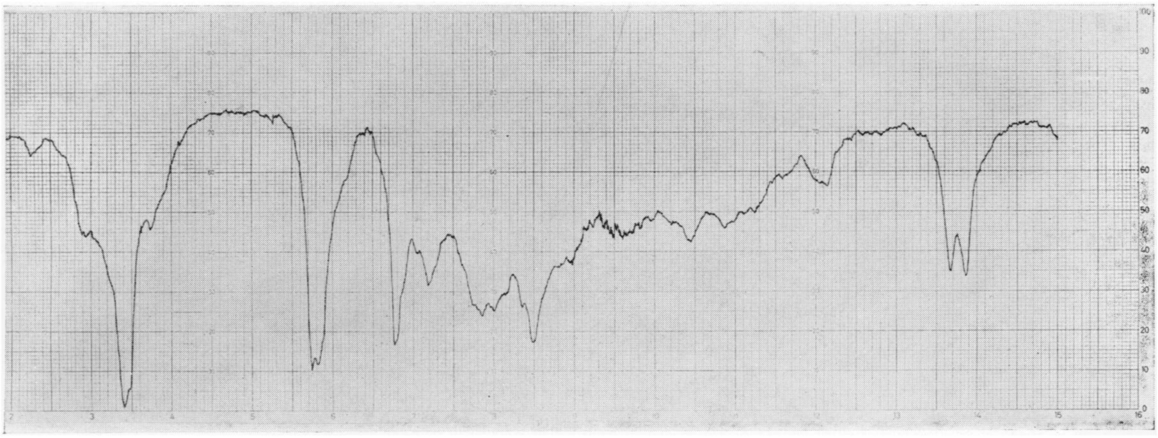

FIG. 5. A relining adhesive composed of beeswax and colophony.

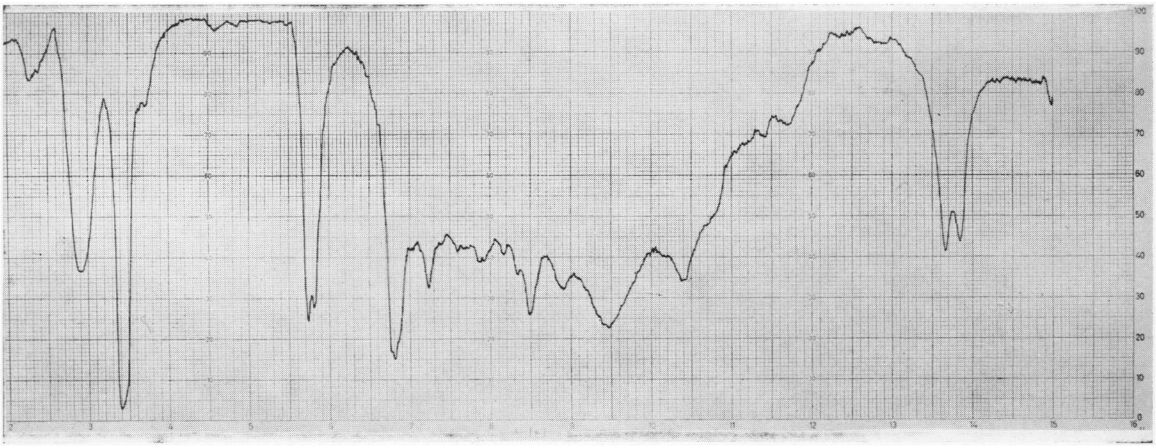

FIG. 6. A relining adhesive of beeswax and A.W.2.

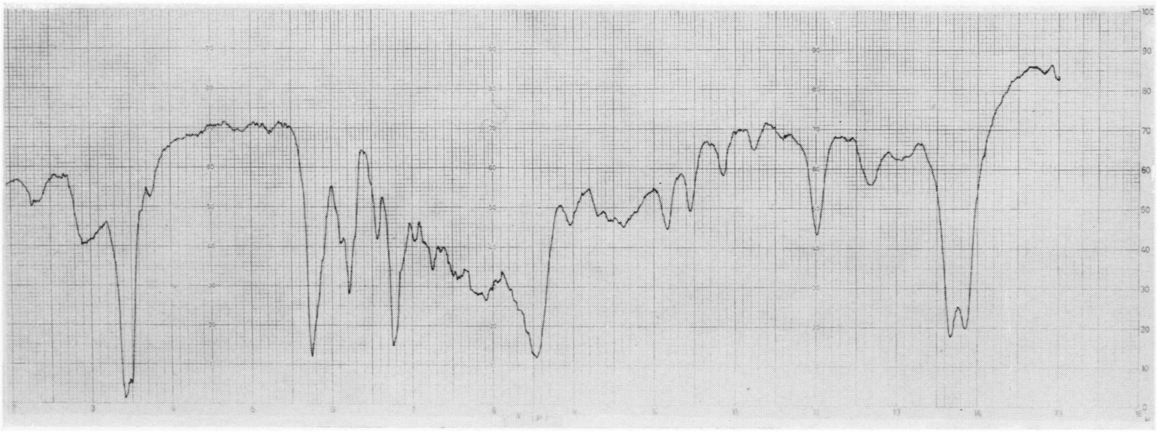

FIG. 7. Carnauba wax.

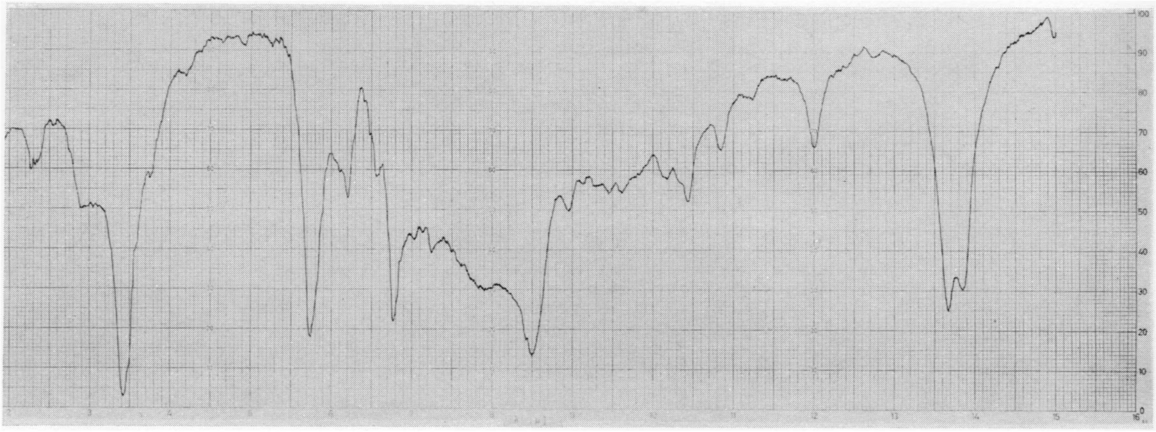

FIG. 8. Esparto wax.

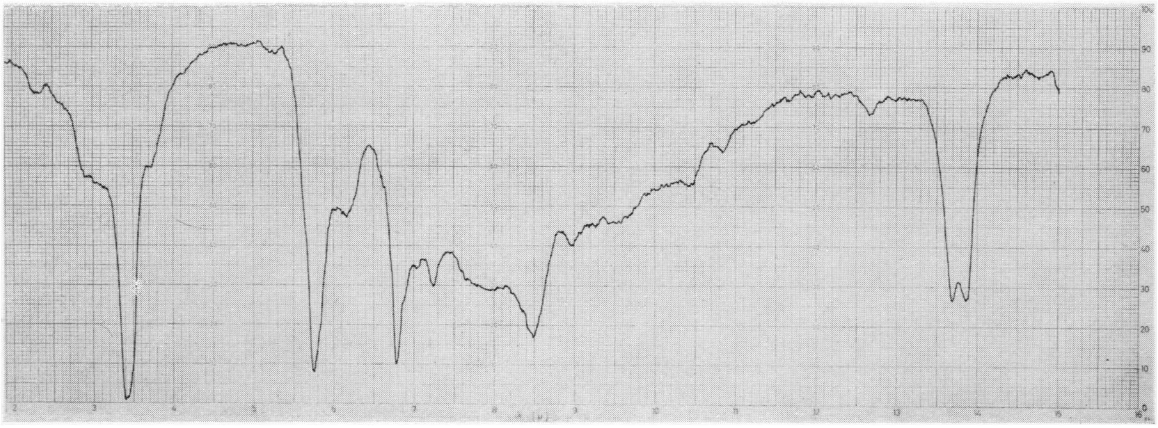

FIG. 9. Crude montan wax.

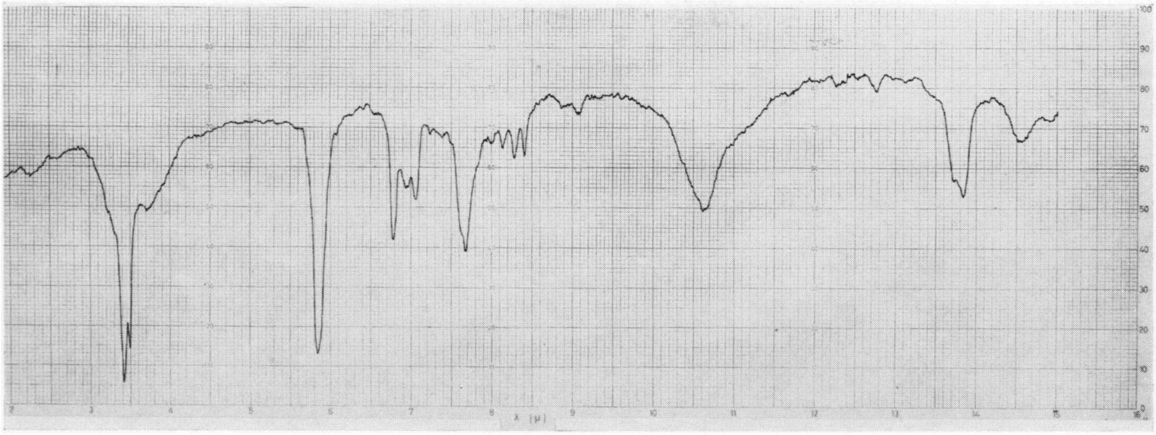

FIG. 10. Stearin wax.

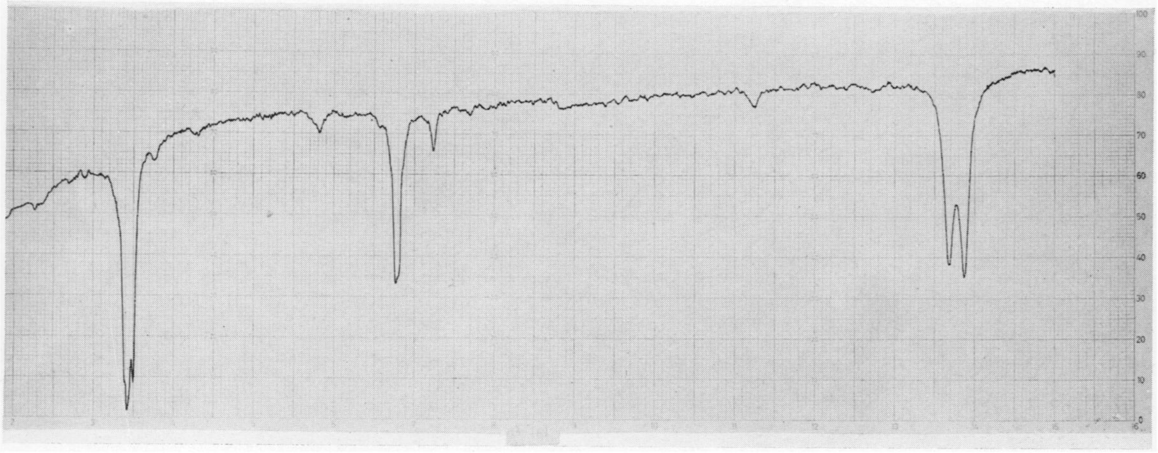

FIG. 11. Paraffin wax.

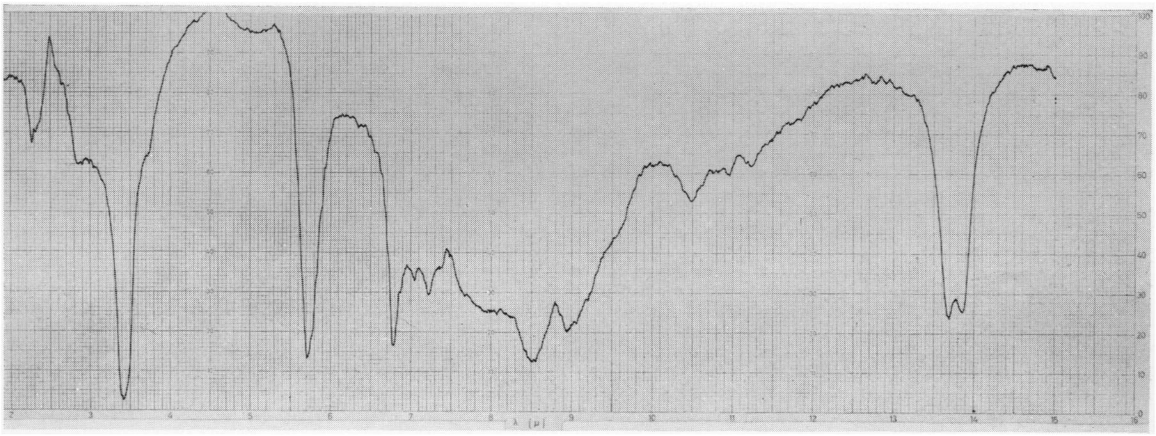

FIG. 12. IG wax N.

and 6·45 μ (1550 cm.$^{-1}$) and near 7 μ (1430 cm.$^{-1}$) [12]. The 6·8 μ band in the beeswax spectrum is broadened by the latter band at the right. Components of the Punic wax soluble in alcohol are given in Fig. 4. There, the beeswax spectrum is weak, since it is less soluble than the soaps. The bands due to ionized carboxylic acids are correspondingly stronger. The residue of an alcohol extraction was pure beeswax as in Fig. 2.

The paint layers of the first two portraits (Fig. 1, *left* and *centre*), which were also extracted with alcohol, showed infra-red spectra similar to Fig. 4 (alcoholic extract of Punic wax). The amount of sample needed for an alcoholic extract is about ten times greater than for a chloroform extract, since Punic wax only contains a small percentage of soaps.

Emission spectroscopy has shown us that sodium is present in all three portraits. The sodium content of the two encaustic portraits seems to be due to the presence of Punic wax. But it is not clear why the tempera portrait (Fig. 1, *right*) contains sodium, and further research will be necessary to clarify this question. Encaustic paintings may contain potassium or calcium instead of sodium, if the caustic agent used was potash or lime. In the mural paintings of Pompeii, lime was used as an emulsifying agent [13].

PAINT MEDIUM IN A SAMPLE OF AN ORIGINAL AND AN IMITATED POMPEIAN WALL

About 50 sq. cm. of the surface of a Pompeian wall-painting were scraped off and extracted with chloroform. The infra-red spectrum indicated beeswax. But this was present in the proportions of only 0·1 of the weight of the pigment (ochre), which would be insufficient to fix it. It is therefore possible that lime also was used, as is described by Augusti [13]. Alternatively, the wax may have been used as a protective coating [3].

E. Schiavi-Gazzola [14], who has developed a new encaustic technique, made a copy of the above Pompeian sample. We scraped off a part of the surface of this copy and extracted the powder with choloroform. The content of paint medium was about 2 per cent. Infra-red analysis gave the beeswax spectrum. However, the infra-red spectrum of an alcohol-water extract indicated a cellulose-ether derivative, probably used as an emulsifying agent.

Comparing the original and the imitated sample by eye, we could not find any difference. But when we scraped off the surface with a scalpel, the paint layer of the original sample looked very dry and powdery, while the imitated sample was a little less lean and less powdery. Besides this, the paint layers of the original and the imitated wall were not alike.

SOME OTHER KINDS OF WAX

Infra-red spectrography may also be used in the analysis of wax in wax-resin canvas-relining adhesives, in putties, or in picture varnishes. Sometimes the sample must first be separated by solvents into its components. In spite of this, an infra-red analysis is simpler and faster, and requires a smaller amount of substance than a chemical analysis. The samples whose spectra are shown in Figs. 5 to 12 were not treated with solvents. They were melted directly on to rock-salt.

Fig. 5 is a mixture of colophony and beeswax used for relining paintings on canvas. Fig. 6 is also a relining mixture consisting, however, of A.W.2 resin and beeswax. The A.W.2 causes a strong band at 2·9 μ (3450 cm.$^{-1}$) [15].

Besides animal waxes, their most important representative being beeswax, there are plant waxes, unknown in Europe until the nineteenth century. One of these plant waxes comes from a Brazil palm and is called carnauba. It is sometimes used by the restorer. This wax is rather hard, and has a melting point higher than beeswax. Its spectrum in Fig. 7 shows, in contrast to beeswax, bands due to aromatic compounds at 6·2 μ (1612 cm.$^{-1}$), 6·6 μ (1515 cm.$^{-1}$) and 12 μ (833 cm.$^{-1}$).

Esparto wax comes from a grass growing in Spain, Sicily, and North Africa. This wax can be easily emulsified. Its spectrum (Fig. 8) also shows bands of aromatic compounds; these are, however, somewhat weaker. Crude montan wax, a fossil wax, is important for the production of half-synthetic or synthetic waxes. It contains many different compounds, so that the spectrum (Fig. 9) only shows broad and diffuse bands. This wax is extracted from lignite.

Stearin and paraffin wax can easily be distinguished from plant and animal waxes. Stearin (Fig. 10) consists of long-chain, free fatty acids with bands at 5·85 μ (1710 cm.$^{-1}$) 10·63 μ (940 cm.$^{-1}$) and between 7 μ and 8 μ.

Paraffin wax (Fig. 11) is a mixture of saturated, long-chain hydrocarbons with bands at 3·4 μ (2850 cm.$^{-1}$), 6·8 μ (1480 cm.$^{-1}$), 7·2 μ (1388 cm.$^{-1}$), 13·7 μ (730 cm.$^{-1}$) and 13·9 μ (719 cm.$^{-1}$). Paraffin waxes are, chemically, the simplest waxes because they contain only hydrogen and carbon, but no oxygen.

Synthetic waxes are another increasingly important group of waxes. Fig. 12 gives the spectrum of IG wax N (new type), which can be emulsified by boiling in water [16]. Synthetic waxes are often preferred to natural waxes, because there are so many varieties of them that one can easily find one with just the property wanted. Synthetic waxes may be based either on pure hydrocarbons, esters, fatty acids, ketones, or on mixtures of these compounds like natural waxes. Thus, nearly all synthetic waxes can be detected and differentiated by infra-red spectrography in the same way as natural waxes.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. H. Lück, Forschungsanstalt für Lebensmittelchemie, Munich, who kindly enabled him to make the spectra. He is also indebted to Prof. Dr. H. W. Müller, Ägyptische Staatssammlung, Munich, for having placed at his disposal several works of art for his studies.

HERMANN KÜHN

Doerner-Institut,
Munich

References

1 Pliny, Book XXI, line 84; and Dioscorides, Book II, section 83.

2 R. J. Gettens and G. L. Stout, *Painting Materials*, New York (1942), p. 80.

3 Called *ganosis*, see Vitruvius, Book VII, chap. 9, pp. 3 ff; Pliny, Book XXXIII, line 122.

4 H. P. Kaufmann and H. G. Kohlmeyer, *Fette, Seifen, Anstrichmittel*, 55 (1953), p. 786; 56, (1954), p. 907.

5 H. P. Kaufmann and J. Pollerberg, *Fette, Seifen, Anstrichmittel*, 58 (1956), p. 974; 59 (1957), p. 815.

6 H. P. Kaufmann and W. H. Nitsch, *Fette, Seifen, Anstrichmittel*, 56 (1954), p. 154; 57 (1955), p. 473.

7 D. Hummel, *Kunststoff-, Lack- und Gummianalyse*, Carl Hanser Verlag, München.

8 T. R. Harkins, J. T. Harris and O. D. Shreve, *Analytical Chemistry*, 31 (1959), no. 4, p. 541.

9 Buberl, *Die griechisch-ägyptischen Mumienbildnisse der Sammlung Th. Graf*, Wien 1922. Christ-Dyroff-Curtis, *Führer durch das Kgl. Antiquarium*, München, 1901.

10 M. Hours, 'Rapport Sommaire sur l'Examen Chimique', p. 23 in *Les Portraits Romano-Egyptiens du Louvre* by E. Coche de la Ferté, Editions des Musées Nationaux, Paris (1952).

11 Pliny, Book XXI, line 84.

12 N. B. Colthup, 'Spectra Structure Correlations in the Infra-red Region', *Journal of Optical Society of America*, 40 (1950), p. 397. Edsall, *Journal of Chemical Physics* 5 (1937), 508.

13 S. Augusti, *La Technique de la Peinture Pompéienne*, Edizione Tecniche, Napoli (1957).

14 E. Schiavi-Gazzola, *Ritrovamento della Tecnica Pittorica Greco Romana ad Encausto, Communicazione tenuta all'Academia di Agricoltura Scienze di Verona nella Tornata*, del 14 Aprile 1957.

15 In Fig. 5 the C-H band of beeswax at $3{\cdot}4\mu$ (2850 cm.$^{-1}$) is broadened on the left by additional OH-groups. Additional carboxyl-groups broaden the ester-carbonyl band at $5{\cdot}75\mu$ (1730 cm.$^{-1}$) on the right. A relatively strong group of bands between $7{\cdot}85\mu$ (1274 cm.$^{-1}$) and 8μ (1250 cm.$^{-1}$) is also caused by additional carboxyl-groups. In this section of the spectrum there is a superposition of bands due to the solid state of beeswax and to carboxyl-groups. A characteristic absorption at 12 – $12{\cdot}2\mu$ (833 – 820 cm.$^{-1}$) is caused by the $R_2 = C = CH - R$ configuration of the resin acids in colophony.

A.W.2 is a condensation product of cyclohexanone and methyl cyclohexanone. Fig. 6 shows, compared with beeswax, a strong band at $2{\cdot}9\mu$ (3450 cm.$^{-1}$), caused by hydroxyl-groups. A band at $9{\cdot}5\mu$ (1053 cm.$^{-1}$) is also characteristic for OH-groups. Additional ketone-groups make the band at $5{\cdot}75\mu$ (1730 cm.$^{-1}$) broaden to the right.

The infra-red spectra of the samples Figs. 5 and 6 show only that the beeswax is not pure. To identify the additional components by infra-red spectroscopy, a separation by means of solvents is first necessary.

UV-absorption spectroscopy is often a valuable supplement to infra-red spectroscopy. Colophony, for example, which consists mainly of abietic acid and its derivatives, shows characteristic absorption in the range 220-280 mμ.

Also the usual chemical tests for resins [*see* H. P. Kaufmann, *Analyse der Fette und Fettprodukte*, Springer Verlag, 1958, p. 1061] should be carried out.

16 IG wax N consists of fatty acids such as montan acid, and of the C_2 and C_4 glycol esters of these acids. It also contains certain natural waxes and an emulsifier whose composition is not disclosed.

L'ÉPREUVE DES CIRES, LA CIRE PUNIQUE COMPRISE, PAR LA SPECTROGRAPHIE INFRAROUGE

Résumé

Contrairement à la spectro-analyse d'émission qui permet l'analyse des pigments, la spectrographie infrarouge fournit la possibilité de déterminer la composition des liants. Cette publication discute la détection de cire, appliquée aux portraits à l'encaustique de Fayûm, et à une peinture Pompéienne. La spectrographie infrarouge donne en outre la possibilité de distinguer la cire d'abeilles de la cire Punique, cette dernière ayant des absorptions supplémentaires de sels d'acides gras. L'essentiel est de pouvoir trouver et identifier une cire à l'aide de la spectrographie infrarouge, même pour des échantillons minuscules. Cela est démontré dans les diagrammes des cires de redoublement, de cire d'abeilles, des cires végétales et minérales et des cires synthétiques.

H. K.