A UNIQUE CEMENT FROM ATHENS

IN 1933 a 5th century bronze head of Nike (Agora Inv. B 30) was found in the Agora at Athens, Greece. Professor Shear in his yearly report 1 commented as follows: "The head from the Agora was cast as a separate unit by the hollow casting process and a considerable amount of the clay core still remained in the interior when it was found." Both Homer A. Thompson 2 and Dorothy Burr Thompson 3 have reported on the head itself but nothing was done about the "clay core" until the autumn of 1957 when Professor Thompson sent us a sample with the request that we examine it to see if we could throw some light on the nature of the core used by Greek sculptors in making a bronze statue.

Preliminary superficial chemical examination showed that the material was not essentially clay although the possibility that some clay might be present was not eliminated. On heating to 105°C the material lost 0.24 percent of its weight and on heating to 900°C, it lost 45.2 percent. Unfired kaolin (China clay), for example, would lose about 14 percent of its weight under similar circumstances while pure calcium carbonate would lose about 44 percent. This high loss on ignition led us to suspect the presence of some organic matter which would burn off at such a temperature. The presence of organic matter was confirmed by a further experiment; 10.1 percent of the "clay core" was found to be soluble in acetone, i.e., it was organic in nature. The actual amount extracted does not have much significance. During cleaning the head was repeatedly soaked in boiling water and considering the nature of the organic matter present, some of it probably melted and may have floated off on the water.

Having separated the original core into two constituents, one organic and the other inorganic, the next step was to identify the materials. The core had a considerable amount of copper in it and also some tin but these constituents could be ignored for our purpose for they undoubtedly had collected there from the bronze head itself during the time it had been buried and also during the cleaning process. Since we suspected that the filler was either lime or clay, we analyzed for alumina and silica (the main constituents of clay) and for calcium oxide and carbon dioxide (the constituents of calcium carbonate). On analyzing the original material we found 2.8 percent silica and 0.7 percent alumina. Since these are present in only minor amounts, it seems safe to assume that they represent small amounts of clay and sand which

¹ Hesperia, II, 1933, pp. 519-527.

² Homer A. Thompson, Harvard Studies in Classical Philology, Suppplement 1, pp. 183-210.

⁸ Dorothy Burr Thompson, Hesperia, XIII, 1944, pp. 173-209.

have deposited on the core or were originally present as impurities. The lime and carbon dioxide, on the other hand, were present in considerable amount: 36.5 percent calcium oxide and 32.6 percent carbon dioxide. The carbon dioxide is present in excess; some of its probably comes from hydrated copper carbonate. As the material is now, it contains over 65 percent calcium carbonate. We believe that it was added as calcium oxide which has become carbonated in the way ordinary lime plaster does. This belief was strengthened by duplicating the mixture with both calcium oxide and calcium carbonate. Calcium carbonate formed a crumbly substance, while, with calcium oxide, we got a rock hard material at room temperature which softened on moderate heating.

The extracted material, after evaporating off the acetone, was pure white and had the unmistakable smell of beeswax. Its melting point was 67.5°C and its refractive index at 75°C—1.442. On analysis it showed 79.64 percent carbon and 13.24 percent hydrogen. The melting point and refractive index are correct for beeswax. The carbon and hydrogen are very close to the mean values for the melissic ester of palmitic acid and other esters present in beeswax plus cerotic acid which are the principal constituents of the wax and which have a mean carbon value of 80.5 percent and a mean hydrogen value of 13.5 percent.

In spite of all these convincing values (as a matter of fact, the odor alone is convincing) we made infrared curves for a modern white beeswax and the extracted material (Fig. 1). The absorption bands for the two are identical; the difference in slope of the two curves is attributable to differences in thickness of the sample films.

It is interesting to note that the beeswax used was highly purified and snow white, not the crude yellow form which is the natural product. This purification by washing, filtering and bleaching ' involves considerable labor and is another indication of the high esteem accorded this piece of sculpture in ancient times.

We next tried to duplicate the mixture using both calcium oxide which would, with time, become calcium carbonate, and calcium carbonate itself. The calcium carbonate mixed with beeswax was crumbly but the calcium oxide-beeswax mixture was plastic when warm and rock-like when cold. We found a ratio of 25 grams beeswax to 45 grams calcium oxide to be satisfactory but of course the amounts could be varied. The above ratio approaches the maximum amount of calcium oxide that it is possible to add to the beeswax; by adding lesser amounts one can make mixtures of varying degrees of hardness.

While it was very unlikely, there did exist a faint possibility that a resistant surface might form on this rock-like material and that it would be possible to use it for a core. We therefore melted some bronze and tried the material for a core but

⁴ H. Blümner, Technologie und Terminologie der Gewerbe und Künste, Vol. II, Leipzig, 1879, pp. 151-163.

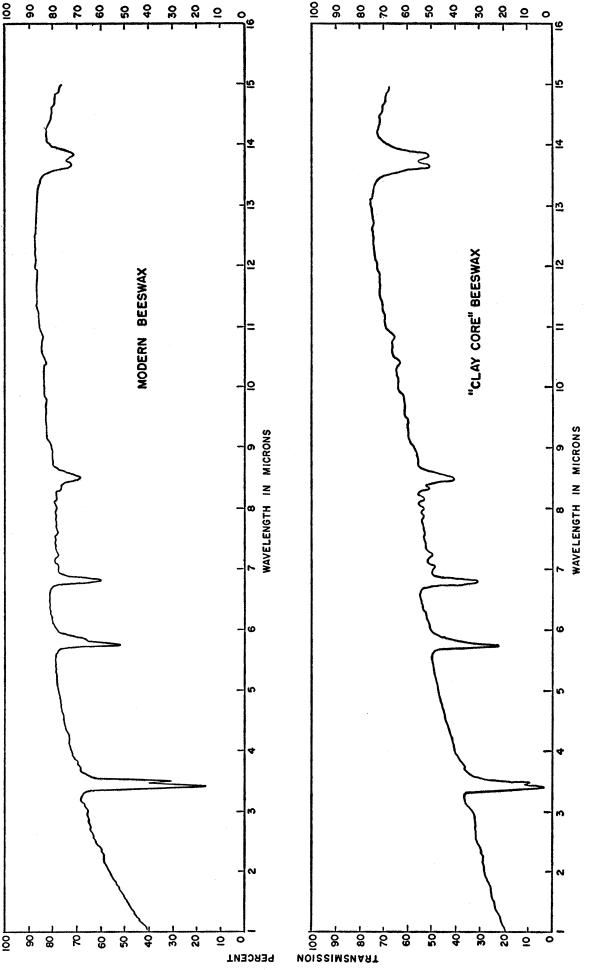


Fig. 1. Infrared Curves of Modern Beeswax and of "Clay Core" Beeswax

the very hot bronze, which melts at around 1000°C, simply went through the wax mixture and melted it with the greatest of ease.

Thompson has discussed the construction of the head and how it was fitted to its torso. He has also discussed the attachment of the gold which was removed periodically for weighing. Although not absolutely necessary, the cement, which could be softened by gentle heat or even by placing it in the Athenian sun, seems to us to be admirably suited for securing the eyes in their sockets and also for strengthening the attachment of the topknot as well as the attachment of the head to its body. A thin application of the wax mixture to the face or even only to the channels around the face would hold the gold firmly in place and yet allow it to be removed easily and without harm, especially after enough heat had been applied to soften the cement. Perhaps the cement was used during its later years but not necessarily when the piece of sculpture was first made.

It should be pointed out, in addition, that the uses for which the beeswax-lime mixture was employed in the examples cited in this paper are remote from the use of beeswax in bronze casting.⁵ There seems to be no valid reason, however, why the material could not be used for this purpose as well as pure beeswax. It would be firmer, especially during the summer months, but would lend itself readily to modelling with slightly warmed tools. When necessary, it could be removed by heating.

In 1955 Miss Talcott had sent one of us (M.F.) a sample of cement which had been used to fasten a Triple Hecate (Agora Inv. S 852)⁶ firmly in a high, square marble base. The context of this sculpture is 4th century after Christ although the statuette itself is probably 1st or 2nd century after Christ. Thus there is a time lapse of several hundred years between these two samples, but still they are very similar in content. The principal difference is that in the Roman sample a part of the lime has been replaced by lead oxide, i.e., we believe it had been added as oxide but it also, like the lime, had become converted into carbonate. This sample analyzed as follows: carbon dioxide—31.64 percent; calcium oxide—39.26 percent; lead oxide—9.32 percent; silica—1.83 percent; iron oxide + alumina—0.63 percent. The rest is organic matter which, when extracted, had the melting point and odor of beeswax. It was not as pure white as the material extracted from the "clay core" but it analyzed 74.28 percent carbon and 13.8 percent hydrogen which is an entirely reasonable analysis for beeswax. Lack of material prevented us from making an infrared analysis but these other values identify it without question as beeswax.

This unique cement has never, we believe, been reported from Greece and is not, in so far as we know, in use today although it has many interesting possibilities. For example, a slightly warmed nail will go through it with ease but will be held with an

⁶ A.J.A., XLI, 1937, p. 183, fig. 8.

⁵ K. Klege and K. Lehmann-Hartleben, *Die antiken Grossbronzen*, Vol. I, Berlin & Leipzig, 1927, pp. 92 ff.

iron grip when cooled to room temperature. We are very grateful to Professor William Bell Dinsmoor for calling our attention to a Mesopotamian analogy where bitumen mixed with calcium carbonate (and clay) was used to cement lion's heads to the temple at Ur. We are grateful to Sir Leonard Woolley for supplying us with the chemical analysis of this material, i.e., the inorganic part of the material, as follows: calcium carbonate (and a little sulfate)—22.4 percent; silica—11.7 percent; alumina (soluble in hydrochloric acid)—4.2 percent; alumina (not soluble)—9.2 percent; lime, etc.—0.7 percent; magnesia—0.2 percent. There is more clay in this material than in the Greek as is shown by the analyses for alumina and silica but it also contains a large amount of calcium carbonate. The Greeks did not have asphalt readily available in the 5th century B.C. and they substituted beeswax. Actually, beeswax seems to us to be suited much more admirably to the purpose for which it was used than asphalt.

On the other hand, resin and also asphalt mixed with clay and lime ⁸ have been reported as fillings, in particular for filling griffin heads of the 7th and 6th centuries B.C. For these examples and also for the Mesopotamian ones, the principal purpose of the filling may have been to strengthen the thin bronze.

The Mesopotamian material is, of course, considerably earlier than even the earliest Greek example. On the question of its date Sir Leonard wrote as follows: "The early Mesopotamian dates are unstable but the average view is that the First Dynasty of Ur, to which the al'Ubaid figures are dated by inscriptions, should be put at about 2700 B.C. and since the temple builder was the second King of that Dynasty a date of approximately 2650 is fairly safe."

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⁷ H. R. Hall and C. L. Woolley, Al'Ubaid, Vol. I, Oxford University Press, 1927, pp. 30-32, pl. X.

⁸ P. Amandry, B.C.H., LXVII-LXIX, 1944-45, p. 62.