with hot dilute hydrochloric acid (1:10), then with hot water, finally once with alcohol. Treat a duplicate filter-paper in the same way, dry both at 100° C. one hour and weigh the precipitate as metallic antimony. Calculate antimony to $Sb_2O_4$, and subtract the same from the weight of mixed oxides of tin and antimony, giving the weight of $SnO_2$ from which tin is calculated.

Copper is usually present in Babbitt and bearing alloys in small amounts, seldom over 1 per cent., and a weak solution of potassium cyanide is used for titrating. One cc. KCN = 0.0025 gram copper.

Results obtained by this method:

SAMPLE NO. 1.

| | 1. Per cent. | 2. Per cent. | 3. Per cent. |
|---|---|---|---|
| Lead | 78.47 | 78.60 | 78.54 |
| Tin | 12.09 | 12.06 | 12.06 |
| Antimony | 9.06 | 9.01 | 9.02 |
| Copper | 0.25 | 0.27 | 0.25 |
| | 99.87 | 99.94 | 99.87 |

Lead by $PbSO_4$ method = 78.55 per cent.

SAMPLE NO. 2.

| | 1. Per cent. | 2. Per cent. | 3. Per cent. |
|---|---|---|---|
| Lead | 68.76 | 68.86 | 68.84 |
| Tin | 15.93 | 15.83 | 15.79 |
| Antimony | 15.02 | 15.10 | 15.04 |
| Copper | 0.14 | 0.14 | 0.14 |
| | 99.85 | 99.93 | 99.81 |

Lead by $PbSO_4$ method = 68.82 per cent.

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## A STUDY OF CERTAIN METHODS FOR DETERMINING TOTAL SOLUBLE BITUMEN IN PAVING MATERIAL.

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THE present paper presents the results of a comparative study of some of the numerous methods proposed for the determination of bitumen, soluble in carbon bisulphide, in the finished surface of an asphalt pavement.

The difficulties encountered in an exact determination have been well set forth by Dow.[1] The first thing to be considered is expressed in his note: "It has been claimed by some that mineral matter (which passes through the filter) is all in chemical combination with bitumen." In order to test this claim (a claim that Dow and other authorities do not endorse) a solution of Bermudez asphalt cement was forced through a Pasteur filter. The filtrate was evaporated in a platinum dish and ignited. The mineral matter left on ignition amounted to 0.06 per cent. of the bitumen taken. This amounts to about 0.006 per cent. of the total paving material as placed in the street, which, as will readily be seen, is an entirely negligible quantity. The following tables give the result of the comparison of the methods used.

The modified Soxhlet method used by the authors was conducted as follows: A piece of hardened filter-paper made by C. S. & S., Düren, No. 575, 11 cm. in diameter, was placed in the center of a cloth having about twice the diameter. The filter-paper and cloth were wet with distilled water and gradually pressed over the end of a test-tube about one inch in diameter, the cloth being outside. The two were held in place by rubber bands and the whole dried at a temperature of 110°. In this way a capsule of hardened filter-paper was prepared. This paper was extracted with carbon bisulphide, dried for one-half hour at 110°, cooled in a weighing-bottle and weighed. A weighed amount of the sample was placed in the filter-paper and the whole inserted into a Soxhlet extractor and extracted until the solvent had siphoned over perfectly colorless for some ten times. The solvent with the extracted bitumen was then ignited in a platinum dish and the percentage of residue determined. The filter-paper and its contents were then dried at 110°, cooled in a weighing-bottle and weighed. The loss in weight less the material recovered from the solvent represented the amount of dissolved bitumen.

The method of Dow is essentially a subsidence method, the details of which are given in the paper previously referred to. The supernatant liquid is finally filtered through a Gooch asbestos filter.

The method used in obtaining the figures in the table headed

[1] Proceedings for the American Society for Testing Materials, Vol. 3, 1905.

"Filtration and Washing on Asbestos Filter" is the method given by Richardson[1] for refined asphalt. It is not recommended by this author for determining the bitumen in the finished paving surface.

In preparing the following tables an attempt was made to show how closely duplicates could be secured, by the various methods, with material supposed to contain 10 per cent. bitumen and which had passed through 1.5 mm. sieve. The first three samples were Malthas and the remainder Bermudez. An attempt is also made to show the relative amounts of fine material recovered from the solvent. This is, however, somewhat uncertain, as the amount of material recovered from the solvent varied somewhat with the size of the sample, the percentage being less with the larger samples. It varied enormously with the thickness of the asbestos mat. The final columns show the percentage of bitumen corrected by deducting the amount of recovered material.

In the Soxhlet method samples varying from 2.7326 to 12.1604 grams were employed. The object was to study whether a large sample tended to give higher or lower results than a smaller one. No constant variation could be noticed but the duplicates do not agree as well as though we had used uniformly about 10 grams, as is generally recommended by the best known writers.

In Nos. 1, 6 and 7, Table III, it is possible that rather thin mats were used. If these were not included in the average, this method would show the smallest percentage of material recovered from the solvent instead of the greatest. It is also proper to state that the material worked with contained occasional small stones. These were difficult to pulverize and thoroughly incorporate into the mass. This explains in part the difficulty in securing exact duplicates in most of the work and especially when small samples were used. It seemed almost necessary in making the determinations shown in Table III to use small samples on account of the difficulty in filtering larger ones.

[1] "The Modern Asphalt Pavement," by Clifford Richardson. Published by Wiley & Sons. 1905. p. 504.

TABLE I.—MODIFIED SOXHLET USED BY AUTHORS.

| No. sample. | Weight of sample. | Per cent. of material recovered from solvent. | Per cent. of bitumen (corrected). |
|---|---|---|---|
| 1..... | 4.4284 | 0.1943 | 10.18 |
| 2..... | 4.4984 | 0.1154 | 10.17 |
| 2..... | 11.1145 | 0.1154 | 9.87 |
| 3..... | 4.5232 | 0.1769 | 9.22 |
| 3..... | 12.1604 | 0.0810 | 9 62 |
| 4..... | 4.5418 | 0.5636 | 9.48 |
| 4..... | 9.0271 | 0.3900 | 9.53 |
| 5..... | 2.7326 | 0.4020 | 10.08 |
| 6..... | 4.3389 | 0.5700 | 10.68 |
| 6..... | 10.4122 | 0.3055 | 10.31 |
| 7..... | 4.4198 | 0.5747 | 9.59 |
| 7..... | 10.4628 | 0.5008 | 9.50 |
| 8..... | 4.2932 | 0.7147 | 9.13 |
| 8..... | 11.4395 | 0.4601 | 9.22 |
| 9..... | 4.2276 | 0.7002 | 9.78 |
| 9..... | 11.3550 | 0.4437 | 9.87 |
| 10..... | 4.7956 | 0.6339 | 9.53 |
| | Mean, | 0.4089 | 9.77 |

TABLE II —METHOD OF DOW.

| No. sample. | Weight of sample. | Per cent. of material recovered from solvent. | Per cent. of bitumen (corrected). |
|---|---|---|---|
| 1..... | 9.9470 | 0.2312 | 10.17 |
| 1..... | 8.4992 | 0.1400 | 10.06 |
| 2..... | 9.8917 | 0.6340 | 9.95 |
| 2..... | 9.4214 | 0.0573 | 10.02 |
| 3..... | 10.1434 | 0.1770 | 9.24 |
| 3..... | 10.0223 | 0.3800 | 9.44 |
| 4..... | 10.0512 | 0.4537 | 9.95 |
| 4..... | 7.4926 | 0.3096 | .... |
| 5..... | 9.9912 | 0.1363 | 9.55 |
| 5..... | 9.1555 | 0.6641 | 9.43 |
| 6..... | 9.9660 | 0.5558 | 10.46 |
| 6..... | 9.9125 | 0.3955 | 10.49 |
| 7..... | 9.9902 | 0.6456 | 9.35 |
| 7..... | 10.5673 | 0.5337 | 9.57 |
| 8..... | 10.0900 | 0.3211 | 9.04 |
| 8..... | 9.5942 | 0.5784 | .... |
| 9..... | 9.9886 | 0.8109 | 9.64 |
| 9..... | 10.0006 | 0.4420 | 9.73 |
| 10..... | 10.1386 | 0.3056 | 9.58 |
| 10..... | 7.3609 | 0.7322 | 9.52 |
| | Mean, | 0.4252 | 9.74 |

TABLE III.—FILTRATION AND WASHING ON AN ASBESTOS FILTER.

| No. sample. | Weight of sample. | Per cent. of material recovered from solvent. | Per cent. of bitumen (corrected). |
|---|---|---|---|
| 1..... | 1.7764 | 1.2180 | 10.76 |
| 1..... | 1.0184 | 1.2000 | 9.50 |
| 1..... | 1.0878 | 1.2170 | 9.55 |
| 2..... | 2.0084 | 0.3711 | 9.84 |
| 2..... | 0.9977 | 0.0200 | 9.84 |
| 3..... | 0.9768 | 0.3798 | 9.58 |
| 3..... | 0.9960 | ..... | 9.67 |
| 4..... | 1.0274 | 0.3018 | 9.76 |
| 4..... | 1.0148 | 0.0986 | 9.92 |
| 5..... | 1.0626 | 0.2164 | 9.80 |
| 5..... | 1.0038 | 0.4583 | 9.06 |
| 6..... | 1.0559 | 1.1960 | 10.14 |
| 6..... | 1.0066 | 1.4900 | 10.78 |
| 7..... | 1.2520 | 2.2720 | 9.88 |
| 7..... | 1.0057 | 0.2980 | 10.62 |
| 8..... | 1.0034 | 0.6870 | 9.98 |
| 8..... | 0.9966 | 0.2308 | 9.34 |
| 9..... | 1.0260 | 0.3059 | 10.21 |
| 9..... | 0.9945 | 0.2513 | 9.91 |
| 10..... | 0.9876 | 0.3745 | 9.80 |
| 10..... | 1.0120 | 0.1778 | 9.79 |
| | | Mean, 0.5926 | 9.80 |

A study of these figures shows the following:

(1) It is very difficult to obtain duplicate results, on account of the difficulty in getting a homogeneous sample of a synthetic mixture like asphalt. There is less variation when large samples are used.

(2) The mean percentage of soluble bitumen shown in the determinations by the method used in Table I was 9.77; by the method in Table II, 9.74; and by the method in Table III, 9.80. This is a remarkable agreement. With the samples used, long subsidence showed no advantage.

(3) As carried out by the authors the modified Soxhlet method shows the smallest percentage of material recovered from the solvent. This is, of course, desirable as it indicates the smallest loss on ignition of organic matter not bitumen, as well as carbon dioxide from carbonates and water from hydrated silicates. The variations, however, are slight and can be overcome by using thicker asbestos mats. This, however, makes the filtration difficult.

The method of Thomas and Dugan[1] was also tested. The only essential difference between their method and the Soxhlet method employed by us is that they use a continuous instead of a siphon extractor, and a soft quantitative filter-paper. We regard both of these variations as less satisfactory than the method employed by us.

The Soxhlet method as given by the authors can be completed within three to four hours from the time the sample is received in the laboratory. The greater part of the solvent can be recovered and used in other determinations. There is a slight tendency for the fine clay to creep upward between the folds of the paper capsule, and a possibility of a trace of clays being left in the siphon tube. In our samples the latter was not noticed except when the extraction was interrupted before completion.

As the method of washing out the bitumen by carbon bisulphide, drying the residue, and igniting the filter-paper apart from its contents, is occasionally used, we decided to conduct a few determinations to determine if an error is introduced by this procedure. The filter-paper was in each case washed with carbon bisulphide and weighed with the usual precautions. After very carefully washing out the bitumen, the filter-paper and its contents were dried and weighed, a correction was made for the mineral matter recovered from the bitumen, and the weight taken by difference. After this weight was obtained, the filter-paper was ignited apart from its contents, the ash from the paper added to the latter and the whole weighed. Starting, then, with a given weight of the sample we obtain two results: (1) the percentage of bitumen when the filter-paper is weighed; (2) the percentage of bitumen when the filter-paper is burned.

| Sample No. | Paper weighed. | Paper ignited. |
|---|---|---|
| 11 | 9.78 | 10.03 |
| 12 | 9.49 | 9.72 |
| 13 | 10.27 | 10.60 |

Thinking that the objection might be raised that possibly the filter-paper holds bitumen in its fibers which cannot be removed by washing, a direct experiment was made by extracting a filter with carbon bisulphide and weighing. This paper was then drenched with a solution of bitumen in carbon bisulphide which

[1] This Journal, **27**, 293 (1905).

had been filtered through a Pasteur filter, and again extracted with pure carbon bisulphide.

Filter No. 1, C. S. and S., 9 cm., No. 597. Increase in weight, 0.0003 gram.

Filter No. 2, C. S. and S., 9 cm., No. 597. Increase in weight, 0.0000 gram.

The higher percentage of bitumen, therefore, shown when the paper is ignited represents a loss of ignited material, *i. e.*, organic matter, carbon dioxide from carbonates, water from hydrated silicates, and probably some bitumen so firmly held by surface tension in the fine clay that it is practically insoluble in carbon bisulphide.

In the following the sample was very finely pulverized during cold weather and mixed with the utmost thoroughness. It is believed that the difficulties of securing a homogeneous sample were thus largely avoided. The results from the sample are as follows:

| | Bitumen. Per cent. |
|---|---|
| Modified Soxhlet | 10.2 |
| Dow's method | 10.1 |
| Richardson's centrifugal method[1] | 10.1 |
| Richardson's filter-paper method (paper weighed) | 10.2 |
| Richardson's filter-paper method[2] (paper ignited) | 10.7 |

These figures seem to us to show that in no case should ignition be resorted to when the analyst is asked to determine the percentage of bitumen in paving material soluble in a given solvent. This, however, does not represent the exact amount of bitumen that was originally brought in contact with the clay as has recently been pointed out by Mr. Richardson in a private communication, for which acknowledgment is here made.

It should be added that Richardson's centrifugal method has given in our hands results practically identical with the results obtained by using the modified Soxhlet or the method of Dow, at a great saving in time.

The writers hope in the near future to repeat some of the work here given, using Trinidad asphalt.

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[1] "The Modern Asphalt Pavement," by Clifford Richardson, p. 541.

[2] Ibid. p. 539.