cents per ton for every 0.25 per cent above 1.50 per cent. The injustice of this practice is very evident as it often happens that coals with a high sulfur content are extremely high in heat value and do not clinker readily at all. Since the sulfur has no appreciable effect upon the metallic parts of the furnace, it need therefore not be considered in the selection of a coal for steaming purposes.

To arrive at the value of a coal for steaming purposes it is therefore just as essential to make the fusing temperature test of the ash as it is to make the calorimetric determination. If these determinations are made an explanation is readily had as to why two coals of apparently like proximate analyses will give entirely different evaporations when fired under like conditions.

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"FREE CARBON"

Its Nature and Determination in Tar Products

By JOHN MORRIS WEISS

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All tars contain a substance in greater or lesser amount, which has been called "free carbon." This has usually been considered as the material insoluble in hot benzol, and is not pure elemental carbon, but a mixture of this substance with insoluble hydrocarbons and other compounds of high carbon content. The amount of this free carbon varies quite considerably in tars from various sources, depending on the original coal and also, to a large extent, on the temperature of carbonization and the degree of superheating to which the developing tar vapors were subjected. Under like conditions, the higher the temperature the greater the amount of free carbon found in the tar produced. The extent to which free carbon varies in tars from various sources may be shown in the following typical analyses of a number of tars:

KINDS OF TAR	Percentage free carbon by toluol-benzol method
Semet-Solvay coke oven.....	10.76
Koppers coke oven.....	6.79
United Otto coke oven.....	13.38
Horizontal retort gas works.....	37.47
Horizontal retort gas works.....	28.91
Inclined retort gas works.....	24.31
Vertical retort gas works.....	3.95
Water gas.....	0.02
Water gas.....	0.38
Oil gas tar.....	1.18
Blast furnace.....	15.89
Lignite.....	1.79
Hardwood.....	0.02
Pine.....	0.03

All these analyses were taken on the dried tars, that is, the samples of tar were distilled until all water was removed, any oil distilling with the water being separated and returned to the distilling vessel after the water was completely driven over.

As stated before, this insoluble material is not pure carbon. One analysis by Donath and Asriel¹ showed

Hydrogen.....	2.3
Nitrogen.....	3.7
Oxygen.....	7.13
Carbon.....	89.2

This analysis adds up to over 100, but the writer can

¹ Lunge's "Coal Tar and Ammonia," 4th ed., p. 241.

give only the figures as found by him in the reference. Hubbard and Reeve¹ have made several ultimate analyses of so-called free carbon, with the following results:

	From	To
Carbon.....	90.17	94.26
Hydrogen.....	2.59	3.31
Oxygen.....	1.81	5.91
Sulfur.....	0.50	1.78
Nitrogen.....	No trace upon a qualitative test.	

They also made analyses of sulfur on various precipitates obtained by digestion of tars with carbon bisulfide for various periods, the results seeming to indicate a combination of tar with the solvent.

One analysis of average free carbon from coal tars made in the writer's laboratory showed

Carbon.....	89.85
Hydrogen.....	3.30
Nitrogen.....	1.10
Oxygen.....	3.13 (by difference)
Sulfur.....	1.28
Mineral ash.....	1.34

The free carbon used for this analysis was obtained by the toluol-benzol method, which is described in detail in a later part of this paper.

Many methods have been proposed for the estimation of free carbon. Kraemer² extracts the tar with forty times its volume of xylol. Köhler³ heats 10 grams of tar with 25 grams of glacial acetic acid and 25 grams of toluol, pours the mixture on two filters of equal weight placed inside of each other, and washes with hot toluol until colorless. Kraemer and Spilker⁴ mix the tar with twenty parts of xylol, filter off the insoluble material, wash with five parts of xylol, and dry on the filter. The same authors give another method which consists of mixing one part of tar with three parts of aniline, pouring the liquid mass on a porcelain plate of special shape. The insoluble carbon remains as a heavy mass after the liquid has been sucked into the porcelain and is removed with a wooden spatula, dried and weighed. The statement is made that this method gives from 2-3 per cent lower results than the xylol method described, due to the greater solubility of the tar bitumens in aniline. Hodurek⁵ has found that some solvents, of which benzol, acetic acid and ether are mentioned, have a precipitating action on bituminous substances, such as those contained in coal tar, and has devised a method based on filtration of the original undiluted tar to determine the real free carbon. The method is, however, cumbrous and not adapted for practical work.

Hubbard and Reeve,⁶ after a comparison of various methods, proposed the use of cold carbon bisulfide as the solvent in testing tars for free carbon. The method was claimed to be equally applicable to both tar and asphalt products. These authors also make mention of the progressive formation of further insoluble matter when the filtrates are allowed to stand,

¹ *Proc. Am. Soc. Testing Materials*, **11** (1911), 665.

² Lunge's "Coal Tar and Ammonia," 4th ed., p. 426.

³ *Z. angew. Chem.* (1888), 677.

⁴ *Muspratt's Indus. Chem.*, **8** (1900), 3.

⁵ *Oesterr. Chem. Zeit.* (1904), 365.

⁶ *Proc. Am. Soc. Testing Materials*, **10** (1910), 420.

and ascribe this phenomenon either to sedimentation or to a combination of tar and solvent. S. R. Church, in discussing this paper, objects to the use of this method for testing tar products, contending that for these materials the use of two solvents is desirable, and that a hot extraction is necessary. The method suggested by him and later published in connection with other methods for testing tars, oils and pitches,¹ involves the use of toluol and benzol, and will be fully described in a later portion of this paper. Later, Church² described an improved form of extraction apparatus, a modification of one proposed for other uses by H. J. Cary-Curr.³

Recently, in a book published by Arthur R. Warnes,⁴ there is described a method devised by Hooper and a modification of same by Warnes. This method involves the use of cresylic acid and 90 per cent benzol, and the writer has had no experience in its use, but objects to 90 per cent benzol and cresylic acid as solvents, because they are not definite chemical compounds which can always be obtained pure.

The remainder of this paper may be roughly subdivided into three parts. The *first* concerns work on the formation of insoluble compounds in mixtures of tar products and various solvents. The *second* comprises a comparison of various methods for "free carbon" or insoluble material determination, the work involved being carried out on a number of materials, both of pitch and asphaltic origin. The *third* portion involves a detailed description of the toluol-benzol "free carbon" method as developed in our laboratories, for tar and tar products, and decided after considerable experience and experimentation as the most convenient.

I—INSOLUBLE COMPOUNDS FORMED IN MIXTURES OF TAR PRODUCTS AND VARIOUS SOLVENTS

The experiments which are set forth in the first part of this communication were originally undertaken for the purpose of obtaining a tar free from insoluble residue, without otherwise changing the chemical constitution of the tar. As will be seen later, the attempts to this end were unsuccessful, but the results were very interesting, and led to the further experiments outlined below.

To remove free carbon, chloroform was first used as a solvent, because its low boiling point renders it easy to remove without superheating. Moreover, it has an odor distinct from that of the aromatic hydrocarbons, and its removal could be more or less accurately indicated by the odor of the residues handled. The tar selected was a coke oven tar, containing about 5 per cent of insoluble matter when tested by the toluol-benzol method. A weighed quantity of tar (about 500 grams) was diluted with about ten times its volume of pure chloroform and filtered twice through weighed thimbles made of a double thickness of S. and S. No. 575 hardened filter paper. When all material had been passed through the thimbles, these

were placed in the extractors and exhausted with hot chloroform. The extracts were refiltered through fresh thimbles, and again extracted. All the thimbles were dried at 100° C. and weighed. The combined filtrates and washings were brought into a tared flask connected to a condenser, and the bulk of the chloroform taken off on a steam bath. The condenser was then disconnected and the material was held at a temperature of 80° C. until it had regained its original weight, less the amount of insoluble matter removed. This latter amounted to 5.54 per cent. At this point, all odor of chloroform had completely disappeared.

This supposedly carbon-free tar was then tested by the toluol-benzol method, and also by a chloroform extraction to determine the percentage of insoluble matter. The results were:

Percentage insoluble in	Original tar	Treated tar
Toluol and benzol.....	5.54	10.05
Chloroform.....	5.36	0.88

The inference to be drawn is obvious. On standing, chloroform formed a compound with the tar which is insoluble in benzol. This insoluble material is quite different in appearance from ordinary free carbon. The latter is dull black, and infusible, while this substance had considerable luster and could be sintered together by careful heating. Under the microscope it appeared slightly crystalline. No quantitative test was made on this substance, but on oxidation with fuming nitric acid, a very strong qualitative test was obtained in the resulting solution.

Following this, a similar amount of the same tar was treated in like manner, using pure benzol (benzene) as the solvent instead of chloroform. The tests of this treated tar were:

Percentage insoluble in	
Toluol and benzol.....	4.71
Benzol alone.....	4.67
Chloroform.....	2.17

This residue also did not resemble ordinary free carbon, being brown instead of black. Under the microscope, it appeared absolutely amorphous. On heating, it melted with decomposition and coking.

Slides were made of the original and treated tars, and viewed in a very thin layer with the microscope by transmitted light. Similar slides were also made, mixing a drop of one of the tars with a drop of the solvent. The magnification used was eighty-seven diameters. This examination confirmed the analytical tests, and threw further light on the subject. The results are given in the following table. The body of the slides appeared a clear, reddish brown, with the variations as noted in the following table.

The apparent meaning of the following results is that in the treated tars there is no real insoluble material of the same nature as ordinary free carbon, but that apparently materials have been formed which, though soluble in the complex mixture known as tar, yet are precipitated upon the addition of a solvent. These results indicate that both chloroform and benzol in contact with tar undoubtedly form compounds with some of the tar constituents, which compounds are at

¹ THIS JOURNAL, 3 (1911), 227.

² *Ibid.*, 5 (1913), 195.

³ *Ibid.*, 4 (1912), 535 and 856.

⁴ Warnes' "Coal Tar Distillation," p. 146.

SLIDE NO.	MATERIAL	APPEARANCE
1.....	Original tar	Very granular with amorphous grains of various sizes.
2.....	Tar treated with chloroform	Clear, without grains.
3.....	Tar treated with benzol	Clear, without grains.
4.....	Mixture of No. 1 and benzol	Strongly granular.
5.....	Mixture of No. 1 and chloroform	Strongly granular.
6.....	Mixture of No. 2 and benzol	Very strongly granular.
7.....	Mixture of No. 2 and chloroform	Nearly clear.
8.....	Mixture of No. 3 and benzol	Granular and slightly crystalline.
9.....	Mixture of No. 3 and chloroform	Granular and fine, needle-like crystals.

least partly insoluble in benzol, and to a lesser degree, in chloroform. These three tars were also tested for fixed carbon and ash.

	Percentages fixed carbon	Ash
Original tar.....	15.42	0.13
Chloroform treated tar.....	14.65	0.02
Benzol treated tar.....	13.78	0.01

These results are also indicative, as the fixed carbon was not lowered as much as would be expected from the removal of over 5 per cent of material nearly all carbon. It would tend to show that simultaneously, higher, more complex bodies were formed which, on heating, give an increased coke residue. Possibly the chloroform may also form bodies of a trialkylmethane series, which would have this tendency to a very marked degree. It was not thought worth while to subject these residues to an ultimate quantitative organic analysis, as with an evident mixture of compounds, such results would show but little.

In the light of the foregoing results, experiments were then instituted to see whether, in the laboratory determination of free carbon, the results obtained would increase with the time the solvent and tar were allowed to remain in contact in the cold. The same tar was used for this work as in the previous experiments. Except for the time of standing with the first amount of solvent added, the general procedure in all cases was identical. In one series of tests, toluol was used as the digesting solvent; in another, benzol. In both cases benzol was used afterward in the extractor.

Time of standing	Percentage insoluble in benzol	Insoluble in toluol and benzol
0.25 hour.....	6.42	5.54
24 hours.....	6.65	6.30
90 hours.....	7.74	7.55
138 hours.....	9.25	8.44
258 hours.....	10.72	9.34

The longer the tar stands, the greater the amount of insoluble residue obtained. The reaction is evidently accelerated by the presence of a large excess of the solvent, and occurs equally with benzol and toluol. With only small amounts of benzol present, such as in an ordinary tar, it is conceivable that this reaction might take place with a very small velocity. In other words, with long time the amount of apparent insoluble matter in a tar might increase.

Experiments were then instituted by the writer to see whether carbon bisulfide and chloroform would give similar results. Tests similar to those with

benzol and toluol were made, using carbon bisulfide and chloroform separately, the material under trial being used both in the digestion and in the extractor. The following results were obtained on the same tar that was previously used:

Time of standing	Percentage insoluble in chloroform	Insoluble in carbon bisulfide
0.25 hour.....	5.91	5.84
48 hours.....	6.93	6.62
120 hours.....	8.27	7.37
216 hours.....	8.01	7.67
288 hours.....	8.21	7.52

A similar increase in apparent insoluble matter was noted here as with benzol and toluol, though not to the same extent.

The residues from the chloroform extraction were tested qualitatively for chlorine with positive results, but as no tube furnace was available, quantitative results could not be obtained. On the other hand, the residues from the carbon bisulfide extractions were assayed for sulfur by the "Eschka" method, the following figures being obtained:

Residue from a	Time of standing	Percentage sulfur
Benzol extraction.....	..	0.92
Carbon bisulfide extraction....	0.25 hr.	1.46
Carbon bisulfide extraction....	120 hrs.	1.82
Carbon bisulfide extraction....	216 hrs.	1.67

This is conclusive proof that the solvents actually enter into combination with the tar constituents. The results can be explained on no other basis.

At various times, the writer has noticed in some of the German publications on tar products, that aniline, pyridine and glacial acetic acid have been suggested as the digestive solvent for free carbon determination. The following results were obtained using the material mentioned for digestion, and then in all cases after filtration, using benzol in the extractor:

Time of standing	Percentage free carbon by digestion with		
	Aniline and benzol	Pyridine and benzol	Glacial acetic acid and benzol
0.25 hour.....	5.00	5.11	6.80
48 hours.....	4.81	5.23	7.01
144 hours.....	4.62	5.27	8.10

Here quite different results were obtained in the case of the first two solvents, aniline and pyridine. Acetic acid gives high results, and shows the phenomenon of progressive formation of insoluble compounds. It was also noted that, owing to its hygroscopic nature, water is easily absorbed and in this event, precipitates are formed which dissolve very slowly in the extractor. The pyridine is a very disagreeable substance with which to work, and is expensive and difficult to obtain in the pure state. The filtration of the aniline solution is a very slow and tedious operation, from four to five hours being required in many cases to pass 50 cc. through the thimble. In spite of the theoretical aspects of the matter, neither pyridine nor aniline seem to the writer to be suitable materials for a laboratory assay of free carbon.

It was then deemed advisable to try further experiments on various tar products. So far, but one tar had been used, and it was possible that this was a

peculiar material, giving rise to phenomena not shown by other similar substances. A series of experiments on various materials was made, comparing aniline and toluol as the digesting solvents, and using benzol afterward in the extractor.

Time of digestion	Aniline		Toluol	
	0.25 hour	72 hours	0.25 hour	72 hours
Coal tar No. 1.....	3.22	3.71	5.09	5.31
Coal tar No. 2.....	12.48	12.83	14.28	17.59
Coal tar pitch.....	8.68	9.08	13.22	15.15
Water gas tar.....	0.02	0.17	0.02	0.19

Besides, several substances were tested at 0.25 hour only, using aniline *versus* toluol:

	Aniline	Toluol
Water gas tar pitch.....	4.11	5.28
Coal tar roofing pitch.....	20.51	25.57
Coal tar briquette pitch.....	17.30	21.13
Coal tar paving pitch.....	13.08	16.72
Road compound.....	11.88	13.95

Various filtrates from this last set of tests were examined under the microscope by the hanging drop method. With both aniline and toluol, the first few drops filtered showed a very faint trace of insoluble matter; the remainder of the filtrate was in both cases perfectly clear when examined immediately. The aniline filtrate remained so, even after twenty-four hours' standing, but the toluol filtrates showed a gradual formation of insoluble matter in the form of amorphous grains. The formation of this precipitate was accelerated by further dilution with either toluol or benzol. The aniline solutions, similarly diluted, also showed precipitation, but of a quite different nature, being in the form of clear, fine, crystalline needles. The toluol filtrates showed precipitation on standing alone, the aniline filtrates only after the addition of benzol.

These results are of the same general nature as those with the first tar investigated. In water gas tar products, where the insoluble residue is very small, the differences between toluol and aniline are not marked. Tar No. 1, which shows no increase on standing with toluol, was unusually high in tar acids, and this factor may be the cause of its variable behavior. With substances varying as much as tars do, it would be too much to expect that all varieties would behave in exactly the same way, and it seems sufficient that a majority of those investigated showed similar phenomena when mixed with various solvents. For a practical laboratory test, neither aniline nor pyridine seem suitable. The latter, as before mentioned, is very disagreeable in its properties, expensive, and difficult to obtain pure. The difficulty of filtration of the aniline solutions is, to the writer's mind, sufficient in itself to exclude it from consideration for such purposes. Such difficulty is not encountered with toluol, carbon bisulfide, chloroform, etc. For a working method it would seem imperative to consider solvents of the general nature of these materials.

II—COMPARISON OF VARIOUS MORE OR LESS WIDELY USED METHODS FOR DETERMINATION OF INSOLUBLE MATTER

A. Cold carbon bisulfide method, using a Gooch

crucible-standard procedure of the American Society for Testing Materials.¹

B. Toluol-benzol hot extraction method, using a cup made of filter paper.

C. Standard A. S. T. M. method, using cold carbon tetrachloride as the solvent.

D. The method used in C was supplemented by a hot extraction with the same solvent.

Besides these tests, another set was carried out, using carbon tetrachloride and cups of filter paper, and running exactly as in the toluol-benzol method. These results are not recorded because the experience was that results obtained by this procedure are not reliable, especially with tar products. After extraction and drying, the thimbles become very brittle and cannot, in many cases, be handled without loss. In some cases, also, with substances low in insoluble matter, an appreciable gain in weight was noted. The hot solvent and bitumen seem to form some compound which attacks the filter paper and causes disintegration. This is probably hydrochloric acid or chlorine compounds of some sort. An acid reaction was noted in the extraction flasks and in the recovery of carbon tetrachloride; the residues in the distillation vessel had a very strong smell of hydrochloric acid. This phenomenon was not exhaustively investigated, so that no positive assertion as to the cause can be made.

In these experiments, eighteen materials, comprising the most common types of pitches and asphalts, were selected and tested by the four methods mentioned above. All tests were made in duplicate, making 144 single determinations. The work was carried out by a single operator, and great care was taken to have as nearly as possible identical conditions in all cases. The solvents used were chemically pure, of the best obtainable grade. Thoroughly average samples of the various bitumens used were taken for the single determinations. In other words, every precaution was taken to eliminate all variations except those inherent in the particular method employed.

The results are given in the following table, two figures being given under each method, and representing the check determinations. The general consistency of the various materials was about 40° Dow taken at 77° F. for five seconds, under a load of 100 grams.

It was necessary in these tests to alter slightly the cold carbon bisulfide method when tar products were being handled. The slow solution of the last portion of these bitumens made complete washing a long and tedious affair. Accordingly, after the bitumen had been entirely brought into the crucible, the washing was carried on until about 150 cc. of carbon bisulfide had been used. The crucible was then allowed to stand over night in a stoppered bottle containing carbon bisulfide to a depth of about half the height of the crucible. Following this digestion, the washing could be completed with the use of 50–100 cc. additional carbon bisulfide. Precisely the same procedure

¹ *Proc. Am. Soc. Testing Materials*, 11 (1911), 245.

	A.S.T.M. method cold CS ₂		Benzol-tol. hot extr.		CCl ₄ cold Gooch		CCl ₄ hot Gooch	
	1	2	1	2	1	2	1	2
Coal tar pitch, horizontal gas retort.	34.76	35.05	34.50	35.30	42.41	42.26	38.77	37.94
Coal tar pitch, inclined gas retort.	32.07	31.95	30.99	30.67	38.22	38.95	34.78	34.85
Coal tar pitch, vertical gas retort.	10.16	10.47	7.80	8.09	17.25	17.50	15.38	15.90
Coal tar pitch, coke oven.	19.83	19.64	20.92	21.31	30.38	31.75	27.24	27.01
Coal tar pitch, coke oven.	17.26	17.47	18.40	18.26	25.97	26.50	23.09	23.41
Water gas tar pitch.	2.02	1.98	4.73	5.19	10.31	10.76	9.02	9.21
Water gas tar pitch.	1.60	1.46	7.92	7.71	14.83	13.31	11.93	11.77
Blast furnace tar pitch.	30.20	29.70	28.76	27.95	34.87	35.32	32.82	32.31
Pine tar pitch.	4.68	4.60	8.00	7.59	11.67	11.47	11.41	10.97
Stearine pitch.	4.61	4.70	(a)	...	...	...	...	...
Bermudez asphalt.	5.49	5.43	5.53	5.70	5.73	5.78	5.61	5.71
Trinidad asphalt.	24.38	24.43	22.21	22.56	23.34	23.89	22.30	21.17
Gilsonite fluxed.	0.14	0.37	0.04	0.07	0.23	0.29	0.24	0.26
Grahamite fluxed.	0.12	0.12	0.0	0.0	0.37	0.32	0.30	0.32
California asphalt.	0.46	0.45	0.27	0.39	0.43	0.41	0.43	0.41
Mexican asphalt.	0.30	0.29	0.57	0.47	0.30	0.40	0.30	0.40
Texas blown asphalt.	1.11	1.33	1.26	1.36	1.13	1.09	0.96	0.96
Texas straight run asphalt.	1.25	1.36	1.71	1.84	1.83	1.51	1.85	1.48

(a) Not considered worth recording.

was necessary when carrying on the cold carbon tetrachloride tests.

Comparing the figures obtained by the hot toluol-benzol method with those of the cold carbon bisulfide method, it will be seen that for the coal tar products in general, approximately the same results are obtained. The one exception is the vertical retort tar pitch, which is notably higher by the cold carbon bisulfide test. The water gas tar pitches give markedly higher results when tested by hot toluol and benzol, a phenomenon which must be explained by the nature of these bitumens, which are quite different from coal tar products. The pine tar pitch is also lower by the carbon bisulfide test in somewhat lesser ratio than the water gas tar products, but nevertheless, striking. All the asphalt products show approximately the same results by both methods, except the Trinidad asphalt, which gives slightly lower figures by the hot extraction with toluol and benzol.

Mention may also be made here of stearine pitch and its behavior in these tests. It dissolves with great difficulty in all of the solvents used, forming gummy masses which were very difficult to filter, and which were broken up only by long washing. The final residue was not "free carbon" in the ordinary sense of the word, but was a somewhat elastic, bituminous mass, which could be melted with decomposition at an elevated temperature. The results with benzol and with carbon tetrachloride on this material were so unsatisfactory and showed such poor concordance that they were omitted as worthless.

The cold carbon tetrachloride test, in all cases on tar products, gave much higher figures than those obtained with the other solvents used. The hot extraction gave lower results than with the cold solvent, but in no case as low as the results with carbon bisulfide or toluol-benzol. On the asphalts there is very little difference between the hot and cold solvent, and only minor variations between this material and the other solvents employed.

The carbon tetrachloride methods have never been considered as basic methods for an insoluble matter determination, but merely as a supplementary procedure to determine something of the nature of the bitumens soluble in other solvents. Therefore, it

would not seem necessary to consider it as a possible solvent for regular "free carbon" tests of tars and pitches. The writer will, therefore, confine himself to a consideration of the relative merits of the cold carbon bisulfide test and the toluol-benzol hot extraction.

On asphalts in general, the Gooch method using carbon bisulfide can be completed in a considerably less time than the toluol-benzol hot extraction, and the results obtained are equally as accurate. For this class of bitumens alone, it seems to be considerably more convenient. But it must not be forgotten that the toluol-benzol method can be used with accuracy on asphalts, and even though it consumes a longer total time, yet the actual time required for the operator is no greater. The extractor, once started, needs no especial attention. The carbon bisulfide cold method is, however, not readily applicable to tar products. It is troublesome and slow. All our experience tends to show that a cold solvent is not desirable for tars and pitches. For these materials, the hot toluol-benzol method is far more convenient and easy of application, and the writer has no hesitancy in recommending it. An aromatic solvent is the natural solvent for tar products, made up as they are of mainly aromatic compounds. Toluol and benzol are aromatic solvents, in fact, the only ones of this series low enough boiling to be applicable to this purpose.

III—"FREE CARBON" METHOD RECOMMENDED

The writer would now turn his attention to a detailed description of the "free carbon" method recommended, using toluol and benzol as solvents. This method in all its essential details has been in use in all of the laboratories of the Barrett Manufacturing Company for a period of years, and has been adopted by a number of outside laboratories. So far as accuracy of results and ease of manipulation is concerned, it has, to the best of my knowledge, given satisfactory results. When the method was first proposed in essentially its present form, check tests on standard samples were made by six of our principal laboratories.

These results seem particularly good when one considers that these tests were undertaken when the method was first introduced, at which time the opera-

Percentages of free carbon in	Coal tar pitch No. 1	Coal tar pitch No. 2	Coal tar No. 1	Coal tar No. 2
Laboratory 1.....	23.40	38.13	28.67	12.24
Laboratory 2.....	24.26	36.44	28.61	13.31
Laboratory 3.....	23.40	39.40	28.80	13.30
Laboratory 4.....	23.41	40.79	29.52	15.26
Laboratory 5.....	24.03	40.71	29.27	13.48
Laboratory 6.....	23.70	38.43	29.49	13.19

tors in the various laboratories were not yet expert in the manipulation of the method. At present, much closer checks could be obtained, and such discrepancies as Tar No. 2, Laboratory 4, would be entirely obviated. Since this time (about five years ago) the principal changes have been in the form of the extractor, the steam bath, and supplementary apparatus. Following the results given in the early part of this paper, the operator should be cautioned against allowing the pitch or tar to digest too long with the toluol. At the outside, thirty minutes should suffice. This feature may have caused some of the discrepancies in check testing on the high side, as at the time of first putting forward this test, the possibility of formation of insoluble compounds was not recognized. All details of the test as standardized today, together with full descriptions of all apparatus used, are included in the following paragraphs.

APPARATUS

The extractor is shown in Fig. I, and is patterned after one described by H. J. Cary-Curr.¹ The principal

FIG. I

requires but little ingenuity on the part of the operator.

Any type of steam or hot water bath will suffice for heating. We have, however, constructed in our own shops a bath for this purpose, which is very satisfactory in operation and, being compact, takes up very little space. It is constructed of copper and consists of a rectangular box eighteen inches long by five inches high. The width varies, depending on the number of extractors to be provided for. For an eight-extractor bath, a width of ten inches would be

¹ THIS JOURNAL, 4 (1912), 535 and 856.

used. Half way up from the bottom of the box is a perforated false bottom, on which the extraction flasks rest. Below this false bottom is a steam coil, entering and leaving through the side of the box. This coil is made of $\frac{3}{4}$ inch copper pipe, strong enough to withstand the local steam pressure. An S bend through the box, giving about 54 inches of pipe, is ample. The top of the box contains two rows of four circular holes each, the openings having a diameter of two and seven-eighths inches. At each corner of the box are uprights carrying a plate of copper the same size as the top of the box, and six inches above it. This plate is cut out with openings directly over those on the top of the box and of the same size, this arrangement serving to steady the flasks. Four condensers are used in series, so that at one end of the box there is provided a water inlet with cock for each row of flasks. The box is filled with water, and the coil keeps this water hot enough to boil the benzol in the extraction flasks. The gradual evaporation of the water is taken care of by a constant level device at the opposite end from the condenser water inlets. The spent water from the condensers drains into this constant level device, and by this means sufficient

FIG. II

water is added automatically to replace that lost by evaporation. There is a draw-off at the bottom of the bath for cleaning purposes. The connections of the condensers are made with rubber tubing. The whole outfit can be placed on brackets on the wall with water and steam connections, and takes up but little space. A picture of one of these baths in use is shown in Fig. II.

The filter cups or thimbles are made of Schleicher & Schuell No. 575 hardened filter paper, which comes in cut circles. The size used is 15 cm. in diameter. To make a cup, two circles should be taken and one cut down to a diameter of about 14 cm. A round stick about one inch in diameter is used as a form. The stick is placed in the center of the circles of filter paper, the smaller inside; the papers are then folded symmetrically around the stick to form a cup of about $2\frac{1}{2}$ inches in length. A very little practice enables the operator to make these evenly and quickly. After being made, they are soaked in benzol to remove any grease due to handling, drained, dried in a steam oven and kept in a desiccator until used.

Besides the apparatus previously described, the laboratory requires beakers, stirring-rods, carbon

filter tubes, and a weighing bottle, all of which are regular stock apparatus. A steam oven for drying is desirable, but an ordinary hot air oven can be made to take its place. A small camel's hair brush or stout chicken feather trimmed down to a fan at the end, should be available as a policeman for removing the last portions of the carbon from beakers.

ANALYTICAL PROCEDURE

If tar is to be assayed, it must be dried before testing, and after drying it is passed hot through a thirty mesh sieve to remove any foreign substances. Pitch requires no previous treatment, other than the ordinary procedure of insuring an average sample. If the pitch is hard enough, grinding the material taken for test will be advantageous in aiding the subsequent solution. In testing materials of 5 per cent or more carbon content, 5 grams should be taken for the test. With lesser percentages, 10 grams should be used. The amount is weighed out in a 100 cc. beaker, and digested with about 50 cc. of c. p. toluol on the steam bath for a period not to exceed thirty minutes. If the solution is kept hot and constantly stirred, the digestion can be completed very rapidly. A filter cup, prepared as described, is weighed in a weighing bottle and placed in a carbon filter tube over a beaker or flask. The toluol-tar mixture is now decanted through the thimble and washed with hot c. p. toluol until clean, using some form of policeman which is unaffected by toluol for the purpose of detaching any carbon which may adhere to the beaker. The cup is finally given a washing with hot c. p. benzol and then, after draining, is covered with a cap of filter paper or alundum, and placed in the extraction apparatus in which the c. p. benzol is used as a solvent. The extraction is continued until the descending benzol is colorless. The thimble is then removed, the cap taken off, dried in the steam oven, and weighed in the weighing bottle after cooling in the desiccator. The balance used for this work should be accurate to at least a half milligram. When pitches are being tested, it is well to examine the carbon residue for foreign matter, such as wood slivers, pieces of bagging, etc. If such foreign matter is present, the test should be rejected. All of the apparatus for this test, with the exception of the special water bath, can be obtained from the Arthur H. Thomas Company of Philadelphia, Pa. This water bath is only desirable if a number of such tests are run as routine work; for occasional tests it would not pay to have one made.

It is the hope of the writer that this paper will throw some light on the nature of "free carbon" in tar products, and that the procedure given here will be useful to the chemist who has occasion to test these materials. He would also express his appreciation of the work of Messrs. L. B. Shipley and C. R. Downs, who performed many of the tests and analyses which are recorded in this paper. One thing which must be kept in mind in free carbon tests as in other analyses of this nature, is that the results obtained are only proximate, and in order to obtain concordant results, faithful attention to details is necessary. We believe

that we have completely standardized all the essential conditions of the test considered, and that it can be applied successfully by workers in general.

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THE RELATION BETWEEN THE MELTING POINT AND THE VISCOSITY OF REFINED TAR¹

By PHILIP P. SHARPLES

The rough dependence of the viscosity of refined tars as determined by any of the standard instruments and their melting point has been long recognized. Many discrepancies have, however, been noted and apparently little thought has been given to the relation between the two in making specifications.

Table I shows a series of samples taken from refined tars made on a manufacturing scale from the same raw tars. The methods used in analysis are those described by S. R. Church in *THIS JOURNAL* 3 (1911), 227 and 5 (1913), 195.

TABLE I—A SERIES OF SAMPLES OF REFINED TAR MADE FROM SAME RAW TAR

Sample No.	Free carbon Percent-ages	Distillation total to 315° C.	Melting point ° F.	Schutte penetrometer		Viscosity Engler 100 cc. at 100° C. Sec.	Float test at 50° C. Sec.
				Sec. at ° F.	° F.		
5	12.1	21.8	...	29	40	94	34
7	12.0	19.2	...	108	40	127	38
8	14.0	16.4	...	114	50	159	58
9	14.4	14.9	86.9	85	60	208	75
10	17.2	12.7	99.7	90	70	335	110
11	18.2	10.4	108.7	88	80	431	170

The melting point is the half-inch cube method in water, starting, however, at 40° F. instead of 60° F.

The Schutte penetrometer is, strictly speaking, not a penetrometer, but a modified melting point. An arbitrary melting point is assigned and the time taken at the assumed melting point to force out under constant pressure a plug of the material cooled to 40° F. is noted. The arbitrary melting point is so chosen on a 10° F. scale that the number of seconds is as near as possible 100.

The float test is the New York Testing Laboratory test. The plug was cooled to 41° F. before floating. The Engler test is made under standard conditions with the exception that 100 cc. were run off instead of 200 cc. The reduction of the number of cubic centimeters with viscous materials allows more concordant results to be obtained and gives lower figures.

A comparison of the three melting points and the Schutte penetrometer figures show that they advance quite regularly together. Other experiments have shown this same relation to hold true, provided the free carbon content is very nearly the same. Samples 7 and 8 may then be included in our further examination of the results without introducing undue error.

An examination of the float test shows an increasing interval between samples as we ascend in the series. Between 7 and 8 the interval is 20 sec. while between 10 and 11 the interval is 60 sec.

The results with the Engler viscosimeter show the

¹ Presented at the Atlanta Meeting of the American Association for the Advancement of Science, January, 1914.