Birmingham Section.

Meeting held at Birmingham University on Thursday, April 14th, 1910.

DR. T. SLATER PRICE IN THE CHAIR.

NOTES ON THE TESTING OF COAL TAR CREOSOTE.

BY J. C. MANN.

Considering the importance of coal tar creosote and the creosoting industry generally one is surprised to find so little information in technical or scientific journals bearing upon this subject.* The pages of our own Journal contain very little information on this particular product. Its importance to the tar distiller may be gauged from the fact that, next to pitch, it is by far the largest of his crude products. I estimate that the annual production in Great Britain from gas works tars alone is about twenty-five million gallons. To this may be added the amount distilled from coke oven tars which probably reaches another ten million gallons. I do not anticipate that the above figures will be increased in the near future, but probably reduced owing to the amount of tar and tar preparations likely to be absorbed for road making.

Recent tests in the United States of the merits of different wood preservatives and methods of application (instituted I believe by the Bureau of Forestry) have placed coal tar creosote in the first rank. The result of this has been to give a welcome demand for the article, the oil being shipped in bulk to the States, the individual cargoes reaching, in some instances, to nearly one-and-a-half million gallons (about 7,500 tons). A considerable quantity is also exported in barrels to Northern Europe, Russia, South America, South Africa and New Zealand. At one time Germany did import, but with the general adoption of coke oven recovery plants the Germans now not only supply their own requirements, but even export. However, it is interesting to know that "English" coal tar creosote holds its own. Our own railway companies consume a large quantity for treatment of sleepers, etc., and to this must be added that used for treating telegraph and telephone poles, for fuel oil, disinfectants and a variety of other purposes.

Although the price of the article is only reckoned in pence per gallon and the market fluctuations by sixteenths of a penny per gallon, buyers and users are very insistent, and rightly so, upon the quality conforming to certain defined specifications. Table I. represents an abstract of six specifications taken at random. Where the maximum amount of water is not fixed, up to 3 per cent. is generally accepted. It will be noticed that these specifications, though varying in text really bear upon the following points:—(1) Water; (2) Phenols; (3) Naphthalene; (4) Heavy coal tar oils. As will be seen, these points are governed by clauses defining:—(1) The maximum percentage of water allowed; (2) The minimum percentage of phenolic bodies to be present; (3) The temperature at which the oil shall remain liquid (or fail to deposit naphthalene) or the maximum amount of naphthalene to be present at a given temperature, generally 15.5° C.; (4) The specific gravity and the maximum amount of distillate to be given at some stated temperature.

To decide these points the chemist resorts to the following operations:—

(1) *Water.* Distillation of a measured quantity (usually 100 c.c.) in a retort until no more water is given off. The distillate is collected in a small graduated cylinder to which has previously been introduced a few c.c. of coal tar naphtha, the latter keeps in solution any

naphthalene that may have come over and enables a clear reading to be obtained.

(2) *Phenolic bodies.*—The total distillate obtained up to 315° C. is washed, by heating and agitating with three successive quantities (30, 20 and 20 c.c. respectively) of sodium hydroxide solution of sp. gr. 1.200. The total solution of the phenols thus obtained is washed with and separated from a small quantity of ether to remove any traces of neutral oils that may be present, then gently warmed on water bath to drive off remaining traces of ether, cooled and rendered slightly acid with dilute sulphuric acid, 1: 3. The acidified solution is transferred to a graduated cylinder and after allowing time for settling the percentage of phenolic bodies is read off. Should the percentage of anhydrous phenols be required, the phenols obtained as above are separated from the sodium sulphate solution, run into a small tared retort, the water distilled off and the anhydrous residue weighed in the retort.

(3) *Naphthalene percentage or liquidity (or depositing) point.*—This point is not always easy to settle. In cases where the specification states "That the oil shall give no deposit" at some given temperature (see table I.), the usual method is to cool the previously liquified oil to the temperature specified and maintain it at that temperature for two hours. Should no signs of crystallisation appear, it is assumed that the oil passes the specification requirement, but I have often come across samples which have given a negative result on first examination or perhaps at several subsequent examinations and a positive result later or *vice versa*. It is highly conceivable that many factors may interfere with the crystallisation of a body like naphthalene from such a complex mixture as coal tar creosote.

Where the specification stipulates the maximum or minimum percentage of naphthalene to be present at 15.5° C. the recognised method to ascertain this percentage is perhaps more definite, but the results obtained, even by the same worker, are by no means concordant; furthermore, the operation is both tedious and unpleasant. It is as follows:—A quantity of the sample conveniently one hundred grammes is cooled to and kept at a temperature of 10° to 15.5° C. for twelve hours to effect crystallisation. The mass is then stirred for the space of two hours and kept at constant temperature at 15.5° C. during that time. It is then turned out on to a linen filter cloth, allowed to drain for a few minutes, roughly squeezed by the hand and lastly pressed in a hydraulic or screw press between folds of absorbent paper (but still in the filter cloth) until it ceases to lose weight. The pressed mass is finally removed from the filter cloth and weighed.

The difficulties in the way of conducting such an operation, especially during the summer months, will be readily understood. Probably due to the manner in which crystallisation takes place, the filtering is sometimes a very tedious operation. It is obviously essential that until all oil has been expressed from the filtered mass that the temperature of 15.5° C. should be maintained. Further, I have found that the temperature at which the oil is kept during the twelve hours, ranging as it may from 10° to 15.5° C. seriously affects the results obtained. This will be seen on reference to Table II.

Altogether, this method is highly unsatisfactory; a more rational, and certainly a more expeditious, will therefore be suggested by me.

(4) *Heavy coal tar oils.*—The specific gravity is taken by any of the recognised methods, a standardised hydrometer being the instrument usually adopted.

With regard to distillation, in some specifications the method and conditions are precisely stated; the size of retort or flask, position of bulb of thermometer, rate of distillation, etc., all being expressly laid down, but in others there is an irritating vagueness, much to be deprecated, when it is taken into consideration that a sample of creosote will give a variation of 5 per cent. and over, in the distillate obtained at 315° C., according as it is distilled in a flask with the bulb of thermometer in line with the side tube or distilled in a retort with the bulb

* Since writing these notes an interesting reprint of a MSS., presented by W. F. Sherfesse, Bureau of Forestry, Manila, Philippines, to the U.S. Forest Service, has appeared in the pages of the *Chemical Trades Journal*.

of thermometer wholly immersed in the liquid. Yet both these methods are adopted by buyers' chemists. It would simplify matters considerably if the details of distillation were at all times given concisely. I have known differences to arise which might have been accompanied by most serious consequences from a financial point of view to one or other of the parties to the transaction had it not been ascertained that the respective chemists were working on entirely different lines.

For some years past I have worked on and used a method for the approximate determination of the amount of naphthalene present at 15.5°C ., which appears to give very satisfactory results. The method is based upon the determination of the rise in temperature due to the latent heat of crystallisation of bodies contained in the distillate. At first I thought it possible to make the determination on a small part of the distillate obtained in clause 4, that is to say the distillate yielded at 315°C . using an aliquot part of the remainder for the determination of phenols, and thereby save a distillation, but although the method worked fairly well when dealing with light creosotes (which practically distilled all over below 315°C .) it was not applicable to creosotes containing a large percentage of heavy oils, the results being much higher than the actual. For the purpose of this determination it was found necessary to carry the distillation further.

FIG. 1

The apparatus used for determining the "latent heat point" is shown in figure 1. It consists of an inner tube, A (10 cms. by 1.5 cms.) provided with a cork through which passes a thermometer, preferably calibrated in 0.2°C , the zero mark being about 5 cms. from the bulb. Tube A is fitted concentrically into tube B (18.5 cms. by 3.5 cms.) by means of perforated cork, this cork also carries a thermometer: the space between A and B acts

as an air jacket. Tube B is fitted into vessel C which may be of any convenient size, the latter acting as a water jacket. B is carried by passing through a disc of wood, D, a strong elastic band is slipped over B after passing through D to prevent D rising when immersed in water contained in C. Disc D requires to be clamped to rim of C and also carries a thermometer. C is provided with a stirrer.

The test is made as follows:—A portion of the sample, about 50 c.c., is distilled from a small retort practically to dryness, or until incipient decomposition of residue is observed, the collected distillate is warmed until wholly fluid and then well mixed. The small tube A is removed from the apparatus and filled about two-thirds with the distillate, and gradually cooled being gently stirred meanwhile with thermometer, until the formation of crystals causes the contents of tube to become opaque, the temperature being noted. The temperature of the water jacket, C, and air bath, B, is then regulated so as to be two or three degrees lower than the opacity point just noted. The contents of A are remelted and again cooled gradually to opacity, any moisture is rapidly removed from outside of A and the tube passed through perforated cock into B, the thermometer in A being adjusted so as to be quite central and about 2 cms. from bottom of tube. The temperature will be noticed to slowly rise, afterwards remain constant for from one-half to one minute, finally falling—the maximum temperature obtained is taken as the latent heat point.

FIG. 2

The curve, figure 2, was obtained in the first instance by adding weighed quantities of naphthalene to various samples of the creosote naphthalene-free at 15.5°C . The ordinates giving the "latent heat point" in degrees centigrade, and the abscissæ the percentage of naphthalene. Since then I have examined many samples and checked the naphthalene figure, to be obtained from the curve by taking the latent heat point against the method given in clause 3, using very great precautions which would make the process practically impossible as a technical method, and have obtained very concordant results.

Tables II. and III. will give some idea of the variation in results obtained by the present recognised method, and of the accuracy of the suggested method. The same creosote was used in all the tests referred to in these two tables.

The results that I have obtained, and the time saved by using it, especially when dealing with salty creosotes, warrant, I think, the publication of this method. If other workers obtain satisfactory results with it coal tar creosote might be valued, so far as naphthalene is concerned,

on its "latent heat point" in the same way as crude carbolic acid is valued on its "crystallising point."

TABLE II. (*recognised method.*)

	1	2	3	4
Minimum temperature obtained during 12 hours crystallisation	10° C.	12° C.	14° C.	15° C.
Pressed naphthalene obtained	21%	17%	10.5%	15%

TABLE III. (*suggested method.*)

	Centigrade.			
	1	2	3	4
Opacity point 7.	20.2	21.0	21.4	20.6
Temperature—water jacket	10.0	10.0	10.0	19.0
air bath	10.0	10.0	19.0	19.0
"Latent heat point"	20.5	20.5	20.2	20.3

DISCUSSION.

The CHAIRMAN said the apparatus used to determine the "latent heat point" was apparently an adaptation of Beckmann's freezing point apparatus. He was not quite certain whether the term "latent heat point" was a suitable one and he wondered whether the author could find a better name.

Dr. R. S. MORRELL wished to know if the amount of naphthalene crystallising out depended on the nature and amount of the phenolic bodies present. He would be glad to hear if Mr. Mann had been able to indicate the cause of the darkening of creosote in the air and to suggest a remedy.

Mr. COLLIS said with regard to the latent point of creosote, that the amount of naphthalene crystallising out would probably vary with the different oils, and again, with the different temperatures. It seemed to him that, if creosotes were obtained from a number of sources, the results would not be concordant.

Mr. WARNES confirmed from his own experience the results as stated by Mr. Mann. Some years ago he had worked with him, and they were exceedingly concordant. The results obtained with different creosotes containing the same percentage of naphthalene were almost identical. If the temperature of 60° F. were used in the air bath and water bath instead of using the opacity temperature, a slight difference was found in those samples which contained a large percentage of naphthalene, and a large difference in those which contained a small percentage of naphthalene. He thought that so long as the worker took adequate precautions, used the same amount of creosote in the tube, and adhered to the method of keeping the air and water baths at a previously arranged standard temperature, the results would be commercially correct. When one considered the length of time that the other and more general process took, the trouble of scraping from the linen the creosote salts, (and, unless extraordinary precautions were taken the method became inaccurate) he thought the new method would find favour because, with little trouble, one could obtain accuracy to within a few per cent. If one used the pressure method, adopting elaborate precautions, filtering through a jacketed funnel, keeping the water at 15° C., and using small quantities, so that one could press rapidly, results were obtained quite comparative with the amount of naphthalene added, and with this test. He hoped coal tar distillers would adopt the method described rather than that of cooling and pressure.

Mr. F. H. ALCOCK asked to what the efficacy of creosote as a preservative was due. Apparently from the specifications read there was not much phenol or naphthalene required. He suggested that shaking up the material with alkali would take out the phenolic bodies. Naphthalene was not soluble in water, but would be soluble in ether. Phenols would be soluble in alkaline bodies, but naphthalene would not. It occurred to him that some such system of analysis would serve for an examination of creosote. With regard to the troublesome system of removing the refrigerated bodies by pressure, the process of scraping the linen to remove the precipitates might be obviated by using some solvent, such as ether, benzene, chloroform, and the like.

Mr. P. L. WHITEHOUSE urged that a simple and easy method for the determination of naphthalene was much to be desired. He would like to know what standard Mr. Mann adopted. He evidently took creosote free from naphthalene at 15° C. and standardised by adding naphthalene to that creosote. If the results were based upon that the total naphthalene would not be given, because creosote at 15° C. was not free from naphthalene. Creosote as a rule had no distinct scientific characters assigned to it. Often there was no test required or only simple ones. It was only in cases where definite tests were required that this method would be useful. Creosote was used for such a variety of purposes, that every buyer had to make his own specification, based on the qualities most useful to him. He would like to know a simple method by which to get out the phenols. Some simple method was desired for determining the "acid" or "total phenol" value of the creosote. It was time some definite tests were made for such things as creosote and tar, and it would be beneficial if definite rules could be laid down for carrying out the work.

Mr. MANN in reply said he would gladly welcome any suggestion for a better term than "latent heat point," but the difficulty was to get a name sufficiently explanatory. In reply to Dr. Morrell he said that he knew of no means by which the darkening could be prevented. As to whether the results obtained were influenced by the amount of phenolic bodies, he would emphasise that the naphthalene point did not represent the total naphthalene present in the oil, but the amount not in solution. As to the relation between phenolic bodies and naphthalene in solution, one could roughly estimate that an oil containing say, 30 per cent. of phenols would throw out about 30 per cent. of naphthalene when these phenols were removed, in other words each per cent. of tar acids in the oil enabled it to carry an equal quantity of naphthalene and remain a clear solution.

The methods of testing quoted in the early part of the paper were taken from standard specifications. He had used the new method with creosotes obtained from Manchester, Yorkshire and Birmingham districts respectively, and the results were fairly concordant. As he had mentioned before, it was the naphthalene not in solution that was determined approximately, and it was this naphthalene that was controlled by the specifications. Most of the creosote shipped to the United States was used by the railway corporations for the preservation of sleepers. The preservative qualities of the various constituents were ably discussed in a paper read at the Institute of Civil Engineers some years ago by S. B. Boulton, than whom there was no better authority on the subject. Naphthalene, apart from any preservative property it possessed, acted beneficially in filling the pores of the timber, although it was probable that the heavy liquid bodies had the greater preservative effect.

The tar acids were removed by washing out with an alkaline solution. His experience was not similar to that of Mr. Whitehouse, who seemed to think that creosote was bought on easy conditions in a free and easy way; he found that when contracts were given hard and fast rules were imposed as to quality and the buyer insisted that the creosote must be delivered in accordance with the specification.

TABLE I.
Various buyers specifications for Coal Tar Creosote.

	Specific gravity.	Phenolic bodies.	Water.	Naphthalene.	To become liquid at	To yield on distillation.
a	1025—1045 at 35° C.	5% minimum	not stated	30% at 15·5° C. maximum	35° C.	4% max. at 170° C. 12% between 170—210° C. 50/80% between 210—270° C. 25/30% above 270° C.
b	1035—1065 at 15·5° C.	6% minimum	not stated	to give no deposit at 4·5° C.	—	not stated
c	1050—1080 at 15·5° C.	6% minimum	maximum	to give no deposit at 24° C.	38° C.	between 22·5% and 27·5% residue at 321° C.
d	not below 1010 at 38° C.	8% maximum	not stated	25% at 15·5° C. maximum	38° C.	40% min. between 205/235° C. minimum 20% Residue 270° C.
e	1050 at 15·5° C.	10% minimum	not stated	to give no deposit at 15·5° C.	—	to distil mostly above 210° C.
f	not below 1015 at 50° C.	6% minimum	not stated	25% at 15·5° C. maximum	40° C.	not stated.

ERRATUM.

In the discussion on "The Corrosion of Industrial Ironwork" (this J., June 15, 1910, p. 659), Mr. John C. Mann was one of the speakers, not Mr. E. A. Mann, as printed.

London Section.

Meeting held at Burlington House on Monday, May 2nd, 1910.

MR. W. F. REID IN THE CHAIR.

THE CRYSTALLINE PRODUCTS OF THE HYDRATION OF PORTLAND CEMENT.

BY E. J. READ, B.A., F.I.C.

It has been known for some time that certain crystalline products are formed during the hydration of Portland cement, and various researches have been published bearing on the subject, amongst which I may mention those of Le Chatelier and Candlot. It has been maintained by some that the setting of cement is entirely due to the formation of such crystals, while others favour a colloidal theory, more especially for the hardening process which follows, but is continuous with the setting. It is not my object to discuss these various theories, but to describe a few results of my own in the hope that they may be of use to others who are interested in the subject.

FIG. 1. × 400.

When Portland cement is gauged with water, lime goes into solution and a layer or skin of calcium carbonate

is formed on the moist surface which protects the interior mass more or less completely from the action of the air. Such a pat of cement, however, is not convenient for the study of the crystalline products of hydration, because of the close proximity of the grains of cement, which does not allow sufficient room for the formation of large crystals, and also from the difficulty which appears to exist in cutting satisfactory sections in which one can assume that there has been no action of the cementing and mounting media.

FIG. 2. × 400.

My method is to prepare a microscope slide of the ground cement using water or lime water as a medium, and ringing the preparation with paraffin wax or some inert cement. In this way the process of hydration can be kept under observation for any desired period of time. It is out of contact with the air, a condition which obtains in the ordinary setting of cement. The proportion of water can be reduced to that which is used in laying a wet concrete, so that such a microscopic preparation should give some idea of what actually takes place during the early stages of hydration of Portland cement.

As the result of the examination of many samples of cement, there appear to be two distinct varieties of crystals which accompany the set. One of these is tetracalcic aluminate, the other calcium sulpho-aluminate. Cements can be obtained showing either one or the other, and in some samples both crystalline forms are in evidence. In addition to these, large irregular crystals of calcium hydrate are formed at a later period.

As stated by Le Chatelier, of the forms of hydrated calcium aluminate which exist, those only need be considered, in connection with the set of cement, which are permanent in presence of excess of lime water. The only one thus permanent is the tetracalcic aluminate, to which Le Chatelier gives the formula $Al_2O_3 \cdot 4CaO$, $12H_2O$. It was obtained by him in the form of spheroidal aggregates of long needles or in compact spherulites.

In my own method of preparing this salt I prefer to use sodium aluminate, prepared in the wet way, by dissolving aluminium in caustic soda solution, as in this way one can prepare an aluminate free from carbonate. On precipitating a dilute solution of this with a clear, hot solution of calcium hydroxide in excess, one obtains on cooling crystals which vary in form, according to the proportion of aluminate, from those obtained by Le Chatelier to regular hexagonal plates, such as are formed during the set of rotary cement.

Fig. 1 shows the precipitated aluminate of lime, Fig. 2 the hydration product of rotary cement. These crystals twin readily through the centre of two opposite sides of

FIG. 3. $\times 400$.

the hexagon forming complex star-shaped aggregates. They are insoluble in concentrated solutions of cane sugar while the lime crystals, which also appear in cement are soluble. So far as optical properties are concerned the natural and precipitated hexagonal plates appear to be identical.

Of the sulpho-aluminate set there are two varieties; one the set which is induced by added gypsum and the other that which occurs in cements made in the old bottle-shaped kilns in which it is produced, in part at least, by the presence of the alkali sulphates and aluminates which these cements often contain. Fig. 3 shows the crystals from a rotary cement which has been slowed by gypsum. Fig. 4 shows a sulpho-aluminate formed by the action of alkali sulphate. In this case the needle-shaped crystals are much finer and more felted together. Fig. 5 is a precipitated sulpho-aluminate of lime of the composition given by Candlot, $\text{Al}_2\text{O}_3 \cdot 3\text{CaO} \cdot 3\text{CaSO}_4 \cdot 30\text{H}_2\text{O}$.

FIG. 4. $\times 400$.

Fig. 6 shows one of the large lime crystals which form later in such microscopic preparations as I have described. They are optically identical with the crystals from a

gauged cement which has been kept under water when every precaution has been taken to exclude carbon dioxide. These crystals are easily detached and obtained

FIG. 5. $\times 400$.

in a sufficiently pure state to be identified as calcium hydroxide.

The microscopic preparations when kept for many months gradually become opaque and dry up by absorption of water. If the slide be then cleared with paraffin oil the

FIG. 6. $\times 250$.

colloidal structure described by Michaëlis becomes evident; the lime crystals are not easily recognised, but the hexagonal aluminate remains in evidence.

DISCUSSION.

Mr. B. BLOUNT asked how the crystals were obtained; was the cement in its powdered state enclosed in a little cell? A matter which presented to him very great difficulty was to cut a section from a piece of set cement and from that to decide what particular compounds were there. That task had baffled his own efforts and those of other petrographical people; in fact, he believed, it had never been done in a fully satisfactory manner.

The CHAIRMAN said it was by grappling with the question in a scientific manner, as Mr. Read had done, that real light was thrown on the actual processes which went on in hardened hydraulic cement. There was certainly great difficulty, as Mr. Blount had said, in cutting sections; but the chief objection had been that people would use water and emery to grind the sections, which was of no use; because the water dissolved a great deal more than was abraded by the grinding. Using ordinary distilled petroleum, he found no difficulty in making sections.

Mr. READ said the cement was put on a slide, and was crystallised in that way with wax round it.