ON THE ASSAY OF CREOSOTE.

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BEING not infrequently called upon for advice as to the most suitable kind of creosote for the preserving of hop-poles and other kinds of timber used agriculturally, I was led to examine a number of different samples of creosote in commerce. The authorized method for the examination of creosote, introduced, I believe, by Dr. Tidy, seemed to afford considerable scope for improvement, and, after some experiment, I have adopted the following method as more rapid in execution and less liable to errors of manipulation :

1. The creosote in bulk is warmed, and well mixed till all crystals of naphthalene, etc., are dissolved.

2. A portion is dipped out into a measuring glass marked at 100 c.c., and thence transferred to the distilling flask. The glass is rinsed out with 5 c.c. of benzene, which is added to the flask. For the distillation I prefer to use a nickel flask, holding about 500 c.c., as a glass flask can rarely be used a second time.

3. To the flask is connected by a cork a straight glass tube of $\frac{1}{2}$ inch bore about 2 feet long, which serves as a condenser. A thermometer reading to 350° also passes through the cork.

4. The condensing tube passes into the receiver, a cylindrical separator of about 300 c.c. capacity, stoppered at the top and terminating in a tap at the bottom. The cylinder is graduated from the tap upwards.

5. The distillation is begun gently, then pushed till a temperature of 325° C. (600° F.) is reached, and maintained till no further distillate passes over. It may be necessary from time to time to warm the condensing tube to prevent it blocking with naphthalene.

6. When no more comes over, the volume of distillate is read off in the receiver, 5 c.c. is deducted for the benzene used, and so the percentage of "residue non-volatile at 600° F." is obtained.

7. To the receiver 100 c.c. of caustic soda solution are now added (alkali of specific gravity 1·2 is specified in the old method, but there is no objection to the use of the alkali of specific gravity 1·3, commonly used for ammonia distillations). The mixture is well shaken and put in a water-oven for an hour at least, being well shaken from time to time. Finally, it is allowed to stand till cool, the volume read, and the greater part of the caustic soda solution is drawn off by the tap. There will be more than 100 c.c., owing to the phenols absorbed.

8. The caustic soda solution is boiled for a few minutes, to expel any traces of hydrocarbon, etc., it may retain, and allowed to cool. When cold, 10 c.c. are withdrawn by a pipette, and run into the bottle of a Leffmann-Beam centrifugal milk apparatus; dilute sulphuric acid is added carefully till the alkali is neutralized and the so-called "tar acids" are liberated, then the bottle is whirled for a few minutes in the machine, allowed to cool, and the quantity of "tar acids" in the neck of the bottle read off. A preliminary calibration of the divisions on the neck of the bottle is, of course, necessary to obtain their value in c.c. From these data the percentage of "tar-acids" in the original creosote is calculated.

9. To the contents of the receiver 100 c.c. of dilute sulphuric acid (1:5) is now added, and the heating and shaking of 6 is repeated. The contents of the receiver are allowed to cool, and the volume of the acid extract is read off (it is greater than 100 c.c., because some of the caustic soda solution was not drawn off). Ten c.c. of this are pipetted off into a Leffmann-Beam bottle, the "tar bases" liberated by alkali, and their volume measured after whirling, just as in the last operation. After correcting for the volume of the acid solution, the proportion of "tar bases" in the original creosote is calculated. The "tar bases" sometimes solidify, making it difficult to read their volume with accuracy.

The disadvantages inherent in the old process are the necessity of complete separation of the oil from the caustic soda solution and of the "tar acids" after acidifying, and the filtration of the latter through asbestos. By taking an aliquot part of the soda solution, the losses inevitable in the attempt to collect the whole of the "tar acids" are avoided, while the use of the small bottle and the centrifugal method enables the "tar acids" to be separated and measured with accuracy and speed. The ease of the method also enables the "tar bases" to be estimated, which is desirable, because of their preservative power. In the old method the distillate, etc., has to be transferred from vessel to vessel four times before it is actually measured as "tar acids"; in the method suggested there is no such transference of a liquid that has to be finally measured.

Example.

Readings :

Distillate	...	...	...	...	66 c.c.	67·5 c.c.
Volume of soda solution	...	...	...	...	110 "	110 "
"Tar acids" in bottle	...	...	...	...	47 "	47 "
Volume of acid solution	...	...	...	...	103 "	100 "
"Tar bases" in bottle	...	...	...	...	15 "	10 "

Calculated :

Residue non-volatile at 606° F.	...	...	...	...	39 per cent.	37·5 per cent.
"Tar acids"	...	...	...	...	9·3 "	9·3 "
"Tar bases"	...	...	...	...	2·8 "	3·2 "

It may not be out of place here to give a brief account of some experiments instituted to ascertain in which constituent of the creosote its preservative power mainly resides, as no sound information seems to be available on the point. The "tar acids" are always referred to in creosote specifications, and they have been supposed to act by combining with albuminoids in the wood; others, again, lay stress on the injection of the heavy oils into the pores of the wood, thus mechanically preventing the entry of water, and therefore of decay; while, again, I find many users of hop-poles prefer "creosote salts," which consist practically of naphthalene.

It was decided to institute some experiments to throw light on the relative preservative powers of the various constituents of ordinary creosote, and the first trial was carried out by Mr. H. H. Cousins, M.A., of the South-Eastern Agricultural College at Wye, upon a good sample of hemp-string, which had an average breaking strain when fresh of 33 pounds.

Lengths of this string were soaked in various extracts from creosote and other pure materials, as set out below, at a water-bath temperature; the string was partly buried for two months in ordinary garden soil, dug up, and its strength redetermined.

The results set out in Table II. gave a low value either to pure phenols or the homologous phenols extracted from commercial creosote by alkali; naphthalene was little better; while the non-volatile portion of the creosote, the "tar bases" extracted from it by acid, and the bone oil, which is rich in similar bases, had preserved the string. It does not, however, follow that string will behave in the same way as wood, and other experiments were begun upon wood. In one set small blocks of wood, sawn transversely to the grain, were soaked for half an hour in 5 per cent. solutions in benzene of the constituents to be tested, the solutions poured off, and the blocks dried. One of my colleagues, Professor J. Percival, then seeded each block with a pure culture of penicillium and also with fragments of rotting wood; the blocks were kept in a moist chamber in the dark. The experiment, however, did not succeed; most of the substances entirely inhibited the growth of penicillium, etc., though the wood was repeatedly seeded, and even streaked over first with a nutrient medium.

In the other trial a series of small rods of deal were carefully selected; they were 8 inches long by $\frac{3}{8}$ inch square, and were soaked in the various materials for one and a half hours at a temperature of 90° C. They were then buried in about three-quarters of their length for ten months in ordinary garden soil, taken up, washed and slowly dried, and then broken transversely under similar conditions, with the result set out in Table III.

The results show that the creosote itself, and particularly the non-volatile constituents, had considerable preservative power, as also had the bone oil; the tar "acids" and "bases" had a real but smaller preservative power; but pure cresol had little or none.

As far as the experiments go, they seem to show that the preservative action of creosote lies in its power to fill the cells of the wood with a fixed moisture-resisting material rather than in any chemical antiseptic action; the preservative qualities of cresol and naphthalene are small, for thin pieces of wood at any rate, because the one evaporates and the other dissolves, leaving the wood open to attack. It also

seems desirable in the commercial examination of creosote to estimate the pyridine "tar bases" and rate them as of equal preservative value to the "tar acids." Further experiments on large pieces of wood are in progress, which I hope to lay before the Society at some future time.

TABLE II.

Breaking Strain of String after Two Months' Exposure (original Breaking Strain, 33 Pounds).

Treatment.	Condition.	Breaking Strain, Pounds.
Untreated	Rotten	0
With "tar acids"	Rotten	0
„ volatile distillate from creosote	Rotten	0
„ phenol	Rotten	0
„ cresol	Rotten	0
„ naphthalene	Partly rotten	3
„ "tar bases"	One in six rotten	16
„ bone oil	Sound	18
„ non-volatile residue from creosote	Sound	16
„ creosote in the cold	— — — — —	4
„ same creosote, hot	— — — — —	13

TABLE III.

Breaking Strain (transverse) of Deal Rods exposed Ten Months (original Breaking Strain, 630 Pounds).

Treatment.	Condition.	Breaking Strain, Pounds.
Untreated	Much decayed	300
"Tar acids"	A little decayed	430
"Tar bases"	Surface good	360
Naphthalene	Surface decayed, sound within	410
Non-volatile residue	Sound	570
Animal oil	Surface fair	440
Creosote	Sound	470
Cresol	Much decayed	230

DISCUSSION.

The PRESIDENT having invited discussion,

DR. LEWKOWITSCH said it seemed very probable indeed that the alkaline solution would contain some proportion of the bases, which it would be important to collect and duly take into account in the analysis.

MR. BLOUNT said that while the methods described in the paper were certainly more refined than the older ones, nevertheless the latter, when properly worked, yielded equally satisfactory results. The practical experiments of the author seemed to indicate that one of the constituents which engineers were most careful to exclude from creosote—namely, the heavy oils—possessed considerable preservative value for wood.

DR. DYER desired to join in thanking Mr. Hall for a very interesting paper. The

latter part of the paper confirmed the views held by the late Dr. Tidy, who used to maintain that a high percentage of tar acids was by no means a necessary index of the preservative properties of creosote. Specifications used to stipulate that not more than a certain proportion of non-volatile matter should be left after distillation at 600° C. ; but Dr. Tidy exactly reversed this, maintaining that at least a certain proportion of non-volatile matter ought to be present. With regard to the determination of the tar acids, he (Dr. Dyer) would like to hear whether Mr. Hall had tried, after exhausting with a large quantity of alkali, subsequently exhausting with repeated small quantities. The usual process was to exhaust with repeated small quantities of alkali, probably for the reason that, although carbolic acid (or phenol proper) dissolved in alkali of any strength, yet the higher acids—cresols, etc.—were singularly capricious, being liable, while dissolving in a certain volume of alkaline solution to separate out if the volume of solution were increased.

Mr. ALLEN said that cresol, the immediate higher homologue of phenol, dissolved readily in a solution of sodium cresylate, so that, if there was sufficient alkali to form sodium cresylate, it would stand dilution without separation, while if there was an insufficient quantity of alkali, the cresol dissolved in it if it was strong, being thrown out of solution on dilution. If sufficient alkali were used, the various tar acids would all dissolve, but not with equal facility. It was a case of fractional neutralization, the phenol going first, as the stronger acid. But if too much alkali were used, probably some of the hydrocarbons would go into solution as well. Creosote was very largely employed for the preservation of timber-piles, piers, etc., exposed under water, which in the tropics were destroyed very rapidly owing to the action of the teredo and other worms. A method was much to be desired for the determination of acridine, which was probably the constituent most objectionable to such animal pests.

Mr. CHAPMAN suggested that the use of cork in place of wood in laboratory experiments such as those which the author had made would probably lead to more conclusive results, owing to the greater readiness with which cork would be penetrated by fungoid growths. The difficulties experienced in determining phenols by extraction with alkaline solutions were also met with in the analysis of essential oils containing phenolic bodies. In the case of clove oil, for instance, the determination of eugenol by treatment with caustic potash solution was vitiated owing to the sesquiterpene, caryophyllene, being also appreciably soluble in the alkaline liquid. With regard to the statement as to the non-occurrence of albuminoids in wood, it was, he thought, a very general belief that, but for the presence of those substances in the wood, the cellulose would undergo little or no change.

Mr. ARCHBUTT said that the author's experiments confirmed the conclusions arrived at by Mr. Boulton, and embodied in a paper read by him before the Institution of Civil Engineers in 1884. Mr. Boulton brought forward a good deal of evidence to show that the value of creosote oil for preserving timber lay in the higher and less volatile fractions, and especially in the tar bases, much of this evidence being based on the experiments of the late Dr. Tidy. That paper led to the abandonment of the late Dr. Letheby's specification, in which the phenol was regarded as the most important constituent, and the substitution for it of Dr. Tidy's specification, in which

a certain proportion of less volatile constituents was required, the exact percentage of phenol being of less importance. Personally he had found no difficulty in using a glass retort over and over again, provided that the distillation was not carried to coking. The advantage of using very strong soda was that, when the soda was mixed with dilute sulphuric acid, a supersaturated solution of sodium sulphate was produced, in which the phenols became insoluble, so that the whole of the phenols were thrown out on adding excess of acid. For removing neutral oils and naphthalene dissolved in the soda, filtration through asbestos had been recommended by Dr. Tidy, but he (Mr. Archbutt) had found it simpler to shake the caustic soda solution with ether. In estimating the tar bases he had adopted the method of distilling a separate portion down to coking and shaking with dilute sulphuric acid. The acid liquid is then evaporated to a small volume, and the bases are thrown up by adding pieces of solid stick soda or potash.

Mr. HALL said that he had a good many times tried the effect of boiling the caustic soda solution, comparing the quantities of tar acids obtained with boiled and unboiled solution; but he had never found any notable difference, though it was possible that differences might occur in some samples, and therefore he had suggested the boiling of the solution as a precaution. He had occasionally tried, after removing everything possible by means of alkali, what could be obtained by means of acid. The effect of second and third extractions with alkali had been tried, but as far as his experience went a single treatment with alkali extracted all the phenolic substances. With regard to the question of the presence of albuminoids in wood, it was very hard to say that anything quite of the nature of an albuminoid existed in wood, but the analogy had been pressed strongly that the preservative power of creosote was due to the sort of antiseptic action which carbolic acid, for instance, had upon a substance like true albumen, namely, coagulation. There was nothing in wood exactly equivalent to true albumen, coagulable by phenol. It was the starch always that was affected. Decay was always quickest in fresh sap wood, where the cells contained a good deal of starch. He had been trying to ascertain how far the fungi penetrated the treated wood, but could not get the fungus to start into the wood except in one case, when it had been saturated with cresol, though where the other materials mentioned were present the growth was arrested at the surface.