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Report On

A PROCEDURE FOR THE ESTIMATION OF META- AND PARA-CRESOLS IN THEIR BINARY MIXTURE AND IN TERNARY MIXTURE WITH GUAIACOL

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ABSTRACT

A method is presented for the accurate analysis of meta-cresol-para-cresol mixtures by freezing-point data. While the basic features of the method are admittedly well-known, the technique presented here is new and is considered an improvement in speed and simplicity over that of the original workers, with also a possible improvement in precision. The use of freezing-point data for the analysis of meta- and para-cresol mixtures containing guaiacol is shown to be valid, and the means by which the entire analysis is obtained from freezing point data plus the guaiacol content, separately determined by well-known means, is presented.

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I. INTRODUCTION

(A) Authorization

1. This work was authorized and carried out under authority of Bureau of Ships Project Order 2349/42 of 1 April 1942, and Project Order 22/43 of July 1942.

(B) Statement of Problem

2. Under the basic problem (c.f. Project Order 2249/42 and 22/43) several possible new sources of phenols and cresols have been investigated. These include studies of several wood tar distillates and cresylic acid fractions derived from pyrolysis of lignite. (The results of this work have been forwarded to the Bureau of Ships earlier.) It was found necessary to devise adequate methods for the analysis of m- and p-cresol mixtures and m-p-cresol mixtures containing guaiacol. This report presents the method developed here for making such analyses. It is believed that the method presented will prove of much value in any field of work where the necessity of analysis of mixed cresols and other related phenolics arises.

(C) Known Facts Bearing on the Problem

3. Cresylic Acid, the fraction of alkali-soluble tar distilling between 175° C. and 230° C. (760 millimeters) has commonly the following components: phenol, the three isomeric cresols, and isomeric xylenols, and some higher phenols, phenol and the three cresols being the most significant products. The fact that three of these four important components are isomerides and homolog of the fourth makes for a great similarity of chemical and physical properties, and narrows considerably the means of separation and estimation. The important physical properties of these so-called tar acids are listed in Table I, below:

TABLE I

Properties of the Coal Tar Acids

Pure Component	b.p.(°C.)	m.p.(°C.)	n_D^{20}
phenol	181°	42°	1.5390
o-cresol	190°	31°	1.5350
m-cresol	202.2°	11°	1.5305
p-cresol	202.5°	34.5°	1.5290
xylenols, boil	209° - 225°		

The boiling point differences are such that by distillation it is possible to separate the following four fractions to the extent of 98% or better: (1) phenol, (2) o-cresol, (3) m- and p-cresols, and (4) xylenols. Discounting the xylenols, the only analysis remaining is that of the binary mixture of m- and p-cresols.

(D) Survey of Methods of Attack

4. Numerous chemical methods have been proposed for estimating the m- and p- compositions of their binary mixture, such as sulfonation, followed by fractional steam distillation of the m- and p-cresol sulfonic acids, selective nitration of the m-cresol (by Raschig), and the formation of unique addition compounds by one of the two cresols, m-cresol with urea, p-cresol with oxalic acid, thereby permitting their separation. All these methods are quite unsatisfactory as analytical methods of analysis, particularly for routine work, where rapidity and a minimum of operations are desirable. In addition to lacking the necessary precision, all these methods are so involved and laborious that the analysis of one binary sample by any of them would require one or two days' work.

5. With regard to a physical method of analysis, one striking difference in the physical properties of m- and p-cresols is in their melting-points. Dawson and Montford obtained accurate melting-point data for various binary mixtures of m- and p-cresols, and from this data constructed the melting-point curve of a series of these mixtures with the melting-point as a function of the para-cresol content of the mixture. They then were able to use the melting point of such a mixture as an index of its composition, by reference to their curve of melting-point data for known mixtures. (For the original work of Dawson and Montford see Journal of the Chemical Society 113 (1918), page 935). The great superiority of this method of analysis by melting-point determination over the chemical ones referred to can hardly be overestimated, both from the standpoint of simplicity and rapidity of operation, and from the standpoint of accuracy and certainty of the results. Consequently, all the work done here was devoted to the confirmation and, so far as possible, the technical improvement of the method of Dawson and Montford.

(E) Statement of the Work done at this Laboratory

6. The investigation and work done here was two-fold in purpose:

(a) Construction of an accurate freezing-point curve for a range of binary mixtures made from pure m- and p-cresols, and verification of the fact that the freezing-point correctly indicates the meta-para-cresol composition.

(b) Development of a freezing-point technique giving wholly reliable determinations of the desired precision (0.05° C.) and at the same time being as simple and rapid in operation as possible without impairment of this dependability and accuracy.

In the investigation of these two factors, it was shown that the freezing-point is a correct index of the m- and p-cresol composition of such binary mixtures and can be accurately determined by simple means.

7. The additional problem of analyzing correctly for m- and p-cresols in mixtures containing guaiacol was encountered, and it was shown that on a molar basis guaiacol is precisely equal in effect to m-cresol with respect to the freezing-point of mixtures with p-cresol, so that the meta-para-cresol analysis by freezing-point data is still valid, the separate estimation of the guaiacol by other well-known means providing sufficient additional information for calculation of the m- and p-cresol contents from freezing-point data.

II. THE ANALYSIS OF BINARY MIXTURES OF META- AND PARA-CRESOLS

(A) Presentation of the Method.

(1) The Nature of the Method Proposed.

8. The method of analysis presented in this report for the estimation of the m- and p-cresol contents of their binary mixtures is fundamentally the method originated and described by Dawson and Montford, namely: The use of the melting-point of the mixture as an index of its composition, arrived at by reference to previously determined melting-point data for known mixtures. It was found in the present investigation that some improvements in the technique of Dawson and Montford were possible to give, without loss of accuracy, an analysis of superior simplicity and speed of operation, thereby permitting the analysis of eight to a dozen samples in a day's time.

9. The one significant change in technique in the present work, making for increased simplicity and speed, is the taking of freezing-points rather than melting-points. The latter determinations require greater time and care, and offer no advantage of any sort over freezing-point determinations. The freezing-point technique is not only much more simple and rapid in operation, but it also gives results that are possibly more reliable. In addition, the freezing-point curve is a straight line and so is more readily determined, i.e., by fewer points, than the melting-point curve, which is not straight.

(2) Description of the Procedure and of the Necessary Apparatus.

10. The necessary apparatus consists of the following equipment:

(a) The freezing-point tube - a 22 by 110 mm. glass test-tube. (5 grams of sample in a 22 mm. tube will just sufficiently cover the thermometer bulb. A tube of larger diameter will mean using more sample, and therefore is less desirable.)

(b) The thermometer - a mercury thermometer graduated from 0° C. to 50° C. in tenths of a degree.

(c) The stirring device - a thin, solid glass rod, with the stirring end bent into a circle (perpendicular to the vertical handle) is entirely adequate; the stirrer is operated up and down by hand.

(d) The cooling bath - a large test-tube or beaker filled with water can be used, but a transparent Dewar bottle is a much better container.

11. The procedure of the analysis is as follows: The sample for freezing-point determination is put into the test-tube, no more sample than enough to cover the bulb of the thermometer resting in the tube being necessary; the tube is placed in the cooling bath (of cold water at about 15° C.), and the sample is vigorously stirred. If solidification does not occur when the sample has become fairly viscous, a crystal of p-cresol is added to start crystallization, which will be rapid if the sample has been supercooled. In this case, the temperature will not usually be the true freezing-point (the maximum temperature at which solidification occurs), but this preliminary result will enable the analyst to adjust the water in the cooling bath to a temperature only about two degrees lower than the true freezing-point. The freezing-point tube is then warmed slowly - by being held in the hand - until only a few crystals remain unmelted. The tube is now cooled slowly by the bath, which has been adjusted to a temperature not more than 2° cooler than the correct freezing-point, and the sample is vigorously stirred continuously. Because of the few undissolved crystals present, the freezing will occur this time with only slight supercooling, and the thermometer will be able to register the maximum temperature rise. The stirring must not cease until, due to cooling by the bath, the temperature begins to fall. The maximum temperature registered during the freezing is the freezing-point. The sample should again be melted by hand warmth and the freezing-point determination repeated, with a cooling bath even closer to the maximum freezing temperature. With the proper technique, determinations on the same sample should check as closely as 0.05° (C.) on a thermometer graduated in tenths.

(3) Discussion of the Technique of the Procedure.

12. While the simple procedure just presented is thoroughly reliable and entirely adequate for correct freezing-point determinations, it must be emphasized that the proper technique and attention to details are essential for such results. The procedure presented above of making a preliminary cooling for the purpose of obtaining seed crystals eliminates the major difficulty of supercooling during the freezing-point determination. The maximum freezing temperature is rather short-lived for mixtures, with the result that if the sample has been cooled to more than 1° below the freezing-point before solidification occurs, the maximum freezing temperature may not be reached. In the procedure presented, seed crystals, obtained

from the sample itself by a preliminary cooling (followed by warming), prevent such supercooling, solidification beginning only slightly below the maximum freezing temperature, which will be easily registered. (Naturally, excessive seeding from an outside source would accomplish this on the first cooling, but such seeding would alter the composition of the sample and hence the freezing-point.)

(B) Operation of the Method.

(1) Experimental Data for the Freezing-Point Curve of Binary m- and p-cresol Mixtures.

13. The following table (II) gives the freezing-point data for a series of m- and p-cresol mixtures, determined by the method presented in the preceding section.

TABLE II

% of p-cresol (in meta-para-cresol mixture)	Freezing-point (°C.)
100% (p-cresol alone)	34.35°
94%	29.65°
90%	26.60°
88%	25.30°
86%	23.75°
82%	20.70°

m-Cresol (alone) freezes at 10.8°

The curve of these data constructed as freezing-points against % of p-cresol is given in Plate I (in the Appendix). It is seen that the curve is a perfectly straight line; its equation is $Y = 0.7600X - 41.65$, where Y = the freezing-point and X = the % of p-cresol in the mixture. (This curve does not exactly check with the m.p. curve of Dawson and Montford (1), their curve being convex upwards.) Melting-points as well as freezing-points of several mixtures were taken, and the fact that the melting-points are greater than the freezing-points for mixtures, especially away from the upper end of the curve representing a single compound (100% para-cresol), was confirmed; but these data are not pertinent to the problem and so are not presented here. The melting-point technique was seen to be much slower in operation and less capable of precise results without elaborate temperature bath contol.

(2) Discussion of Necessary Calculations (in obtaining the m- and p-cresol compositions from freezing-point data).

14. Clearly the composition of a mixture consisting solely of m- and p-cresols is known as soon as its freezing-point is known, since by the curve in Plate I the freezing-point is correlated

directly with the % p-cresol in the mixture; the difference of the % p-cresol from 100% is the % of m-cresol. However, this direct approach is not feasible for mixtures containing much more than 20% m-cresol, and therefore melting much below 20° C., the low end of the freezing-point curve in Plate I. The curve has not been extended lower because of the difficulty of determining at room temperature with an accuracy of 0.05° freezing-points much below 20° C. This is particularly so because the maximum freezing temperature is shorter lived as the p-cresol content decreases, and is quite short lived for para-cresol contents much below 80%.

Consequently, for mixtures having more than 20% m-cresol, and therefore freezing below the low end (19°C.) of the curve, the following procedure of analysis is resorted to: Enough pure para-cresol is added to the unknown sample to raise the freezing-point of the new mixture to some point on the curve (that is, above 19° C.). From the final freezing-point the final composition is obtained, and from the amount of pure p-cresol added to the known amount of original sample, both having been weighed to 1 mg., the composition of the original sample is readily calculated. The following example will make this clear: To 6.000 gm. of a mixture X (to be analyzed) are added 12.000 gm. of pure p-cresol (f.p. = 34.3° to 34.4°). The resulting mixture, Y, has a f.p. of 24.90°, indicating (see Plate I) that the composition of Y is $\left\{\begin{matrix}88.8\%\text{ p-cresol, and}\\11.2\%\text{ m-cresol.}\end{matrix}\right\}$. Since only p-cresol was added to X in making Y, the absolute amount of m-cresol is the same in X and Y, being 11.2% of the 18.000 gm. of Y, or 2.016 gm. This 2.016 gm. of m-cresol was originally in 6.000 gm. of X, so that X was $\frac{2.016}{6.000}$ x 100% = 33.6% of m-cresol, and consequently was 66.4% p-cresol. More compactly expressed, the % m-cresol in Y x $\frac{\text{wt. of Y}}{\text{wt. of X}}$ = the % m-cresol in X; thus, $\frac{\text{wt. Y}}{\text{wt. X}}$ x % m-cresol in Y = $\frac{18.000}{6.000}$ x 11.2% = 33.6% m-cresol in X, in the above example. Consequently, the necessity of weighing the sample and the pure p-cresol added is the only additional step (other than calculation of the result by the ratio of the weights, as shown) in analyzing low-freezing meta-para-cresol mixtures. With a supply of pure (high-freezing) para-cresol on hand, any meta-para-cresol mixtures can be analyzed by freezing-point determination.

(3) Reproducibility

15. The reproducibility of the freezing-point is within 0.05° and yields an analysis of the desired precision.

(4) Facts Pertinent in the Operation of the Method

16. It is important to note one fact: The freezing-point of the p-cresol on hand may not be 34.35°, corresponding to 100.0% p-cresol on the predetermined freezing-point curve. If the p-cresol freezes between 34.0° and 34.5°, correct results can be obtained merely by adding to or subtracting from, as the case may be, the difference between the freezing-point of the p-cresol used and the

freezing-point (34.35°) upon which the correlation curve is constructed. In all cases this simple correction gives the correct results, and it was found that the entire curve for p-cresol freezing at 34.5° is parallel to the one for p-cresol freezing at 34.2°, the 0.3° difference being maintained at 80% p- and 90% p- as well as at 100% p-. The curve presented here is actually constructed upon p-cresol freezing about 0.25° lower than much p-cresol purified in this work, since with the correction mentioned this lower curve is fully as valid as a higher one from slightly better p-cresol, and p-cresol freezing at 34.3° is obtained more easily and in larger yields than 34.5° p-cresol.

17. The best results will be obtained if the freezing-point of the mixture taken is between 83% and 93%. Consequently, para-cresol should always be added to samples freezing lower than 20° or 21° C., and the analysis of the original sample obtained by calculation rather than attempting lower freezing-point determinations and extrapolating the straight line freezing-point curve to obtain the composition.

An upper limit of 93% p-cresol is suggested for low freezing mixtures because the more p-cresol that is added to the mixture the more an error in the analysis is magnified with respect to the original meta- and para-cresol composition.

III. THE DETERMINATION OF META- AND PARA-CRESOLS IN TERNARY MIXTURES WITH GUAIACOL.

(A) Statement of the Problem

18. Guaiacol is a component of the meta- and para-cresol fraction from wood tar distilates and is unseparable from the cresols by fractional distillation (guaiacol boils at 205°, p-cresol at 202.5°, and m-cresol at 202.2° C.). Guaiacol can be estimated (quantitatively) in this mixture by the Zeisel methoxy analysis, in which hydriodic acid is used to cleave the ether group of the guaiacol (o-methoxy phenol). (For details see Scott's Handbook of Analysis, Vol. II.) A means of estimation of the m- and p-cresol contents in this ternary mixture without separation from the guaiacol is desired.

(B) Presentation and Verification of the Method of Analysis Proposed.

(1) Theoretical Considerations

19. No previous attempt to solve this problem seems to have been made. Since phenol and o-cresol as well as m-cresol decrease in a regular way the freezing-point of p-cresol in proportion to their concentration in binary mixtures with it, the logical attack was to determine what effect guaiacol mixed in various proportions with p-cresol would have on the freezing-point of the resulting mixtures.

(2) Experimental Basis of the Method: Freezing-Point Data on Mixtures Containing Guaiacol.

20. When mixtures of guaiacol and p-cresol are made up in the range from 80% to 100% p-cresol and the freezing-points are found, these data plotted as freezing-point/weight % of p-cresol are seen to lie on a straight line above the straight-line curve for meta-para-cresol mixtures (of section II). The slopes of these two lines are such that it appears that guaiacol is only about 0.863 as effective as an equal weight of meta-cresol in lowering the freezing-point of p-cresol. This factor 0.863 is almost exactly the ratio of the molecular weight of m-cresol to that of guaiacol, and consequently guaiacol effects the same lowering of the para-cresol f.p. as meta-cresol does, mol for mol. Therefore, if for the above-mentioned guaiacol-para-cresol mixtures the % of p-cresol is calculated on a molar basis - by multiplying the weight of guaiacol by 0.863 (thereby expressing it as its equivalent weight of meta-cresol) and using this modified "weight" in calculation of the percentage composition of the mixture - the guaiacol-para-cresol data, now expressed as freezing-point/mol % p-cresol, lie precisely on the meta-para-cresol curve, as Table III of these data shows.

TABLE III

Composition of Mixture	(1) Weight % of p-cresol	(2) Mol. % of p-cresol	(3) Freezing-Point (°C.)	(4) Corr. % p-cresol on meta-para-cresol curve
0.4101 gm. guaiacol 4.6033 gm. p-cresol	91.8%	92.9%	28.70°	92.5%
0.6075 gm. guaiacol 4.4117 gm. p-cresol	87.9%	89.4%	26.25°	89.3%
0.8111 gm. guaiacol 4.1958 gm. p-cresol	83.8%	85.7%	23.35°	85.5%
1.0148 gm. guaiacol 3.9941 gm. p-cresol	79.5%	82.0%	21.00°	82.5%

It is evident that columns (2) and (4) correspond well (while (1) and (4) do not), which shows that, on a molar basis, guaiacol is exactly equivalent to meta-cresol in terms of freezing-point lowering of p-cresol. Therefore, the meta-para-cresol curve can be used for the correct analysis of guaiacol-p-cresol mixtures, the results being in terms of mol %, from which the composition in weight % can be calculated.

As further proof of the molar equivalence of guaiacol and meta-cresol, ternary mixtures of these with para-cresol were made up and the freezing-points determined. The data (in Table IV) show, as in Table III, the good correspondence of the results on a mol % basis between the ternary mixtures containing guaiacol and the simple meta-para-cresol mixtures.

TABLE IV

Composition of Mixture	Mol % p-cresol	Freezing-Point (°C.)	Corr. % p-cresol on meta-para-cresol curve.
0.4951 gm. guaiacol 0.5082 gm. m-cresol 4.9480 gm. p-cresol	84.1%	21.85°	83.8%
0.2263 gm. guaiacol 0.3914 gm. m-cresol 4.4104 gm. p-cresol	88.2	25.15°	87.9%
0.1968 gm. guaiacol 0.2080 gm. m-cresol 4.5953 gm. p-cresol	92.4%	28.40°	92.2%

(C) Operation of the Method: Discussion of the Necessary Calculations.

21. The experimental results in Tables III and IV show that the presence of guaiacol does not invalidate the estimation of meta- and para-cresols from freezing-point data, since the guaiacol simply influences the freezing-point as an equivalent (molar) amount of meta-cresol, and consequently shows up as such in the resulting analysis. The freezing-point indicates the mol % p-cresol in the mixture; the difference of this value from 100% is the sum of the mol % of guaiacol and m-cresol present, i.e., the "total equivalent meta-cresol" content (in mol %). The guaiacol composition, however, is determined separately by Zeisel methoxy analysis. This weight % value for the guaiacol composition is multiplied by 0.863 to express it as mol %, i.e., in terms of its equivalent amount of meta-cresol. The actual m-cresol composition (mol %) is therefore determined, being the difference of the "total equivalent m-cresol" value and the part of it which the Zeisel analysis has shown to be guaiacol (but expressed on an "equivalent m-cresol" basis). The essence of the calculations is that the weight of guaiacol be expressed as its equivalent weight of m-cresol, by being multiplied by 0.863. This puts the calculations on the molar basis to which the freezing-point is related. Consequently, when the weights of the cresols are added to this modified weight of guaiacol, the calculations are made in terms of "cresol equivalent weights" throughout, or more simply on a molar basis, which the modified weights now represent. The involved nature of the calculations will best be made clear by an example:

Let primed letters stand for (true) weights and unprimed letters stand for "equivalent cresol weights".

(a) The Data:

(1) The freezing-point of the final mixture Y = 25.40° C., which means that Y = { 88.25% para-cresol, and 11.75% "total equivalent meta-cresol" }

(2) 1.0181 gm' of the original mixture X' plus 4.0100 gm' of pure p-cresol gave 5.0281 gm' of the final mixture Y' above.

(3) Zeisel analysis shows the original mixture X' to be 22.22% guaiacol.

(b) The Calculations:

(1) 22.22% guaiacol in 1.0181 gm' of X' = 0.2263 gm' of guaiacol, g', in X'.

(2) Now this weight, g', is multiplied by 0.863 to express it as its equivalent weight of m-cresol: 0.2263 gm' of g' x 0.863 = 0.1954 gm. of g, the "equivalent cresol weight" of the guaiacol known to be present.

(3) It is therefore seen that converting the weight of guaiacol to its "equivalent cresol weight" results in a loss of 0.2263 - 0.1954 = 0.0309 gm. in the figure expressing the amount of guaiacol. Consequently, this difference must be maintained in expressing in "cresol equivalent weights" the weights of all mixtures in which this quantity of guaiacol is present, namely X' and Y'.

(4) Therefore, X, the "cresol equivalent weight" of X', is 1.0181 gm' - 0.0309 = 0.9872 gm.

(5) Likewise, Y, the "cresol equivalent weight" of Y', is 5.0281 gm' - 0.0309 = 4.9972 gm.

(6) But from the freezing-point (see (a)), Y is 11.75% "total equivalent m-cresol".

(7) 11.75% of the 4.9972 gm. of Y is 0.5868 gm. of "total equivalent m-cresol" in Y.

(8) But 0.1954 gm. of this is guaiacol (see (2)). Therefore, the actual m-cresol content of Y is 0.5868 gm. - 0.1954 gm. = 0.3914 gm. This is also the m-cresol content of X (since only p-cresol is added to X in preparing Y).

(9) The amount of p-cresol in X is the total weight of X minus the "total equivalent meta-cresol" content (the same in X and Y, since only p-cresol is added to X to give Y). Therefore, 0.9872 gm. - 0.5868 gm. (from (7)) = 0.4004 gm. of p-cresol in X.

(10) The original mixture is now completely known, and its composition in weight % is readily calculated from the true weight of guaiacol, 0.2263 gm. (from (1)), and the weights of m-cresol and p-cresol found in (8) and (9) (the cresol weights being identical in both systems).

(c) The Analysis is, therefore:

0.3914 gm.	of m-cresol, or	38.45% meta-cresol (by wt.)
0.4004 gm.	of p-cresol, or	39.35% para-cresol (by wt.)
0.2263 gm.	of guaiacol, or	22.2% guaiacol (by wt.)
1.0181		100.0%

IV CONCLUSIONS

(A) Summary of Main Features of the Method

22. It is believed that there has been developed an accurate yet very rapid and simple method for analyzing mixtures of m- and p-cresols and such mixtures containing guaiacol. The freezing-point of the mixture is shown to be a reliable index of para-cresol concentration, regardless of the presence of guaiacol. Separate estimation by Zeisel methoxy determination of the guaiacol, if any is present, permits the calculation of the m-cresol content by difference. The necessity of putting all calculations on a molar basis is shown from experimental data, and the calculations are discussed in detail. (This is only important when guaiacol is present, since m- and p-cresols are isomers.) The technique presented of making freezing-point determinations yields results with an accuracy better than 0.05° C. The necessary apparatus is simple, and is readily constructed from glassware found in any laboratory; the recommended thermometer is easily obtainable. The curve of freezing-point as a function of the p-cresol composition is given for the analysis of m-cresol-p-cresol mixtures containing from 80% to 100% p-cresol. For the analysis of mixtures containing less p-cresol, one needs only a supply of pure p-cresol. This is added to the sample until its p-cresol composition gives a freezing-point on the curve. From the final composition determined by the freezing-point the original composition is readily calculated from the weights of the original sample and of the p-cresol added.

(B) Facts Established

23. Mixtures of m- and p-cresols and such mixtures containing guaiacol can be correctly analyzed with high precision and accuracy

from freezing-point data or from freezing-point data coupled with Zeisel Methoxy Determination (in the presence of guaiacol).

24. The very simple and rapid procedure of freezing-point determination presented is entirely adequate and reliable for freezing-point determinations correct and reproducible within 0.05° C.

(C) Recommendations

25. It is recommended that this method be used for the analysis of appropriate cresylic acid fractions when it is desired to know the composition of the mixture with respect to the isomeric m- and p-cresols (and guaiacol). This procedure should lend itself to the control of the composition of cresols for antiseptics, or raw material for the manufacture of plasticizers, for cable insulating stocks or synthetics. It has already proved to be of value in the exploration of new sources of phenol and cresols.

APPENDIX A: Purification of para-cresol and meta-cresol (for Freezing-Point Work).

For the preparation of high-freezing p-cresol, crystallization from ASTM petroleum naphtha gave excellent results. This solvent proved more effective than anything else tried. The ratio of naphtha to cresol is 2:1 to 1:1, depending upon the purity of the commercial cresol. The solution is cooled to about -5° C. by adding dry ice, and is then seeded with p-cresol (of any purity, previously frozen by dry ice). Crystallization should occur between -5° and -10° and should be fairly gradual, or else much solvent will come out with the p-cresol. When the crystallization is slowly done, as little as 15 cc of solvent in 200 cc of p-cresol will be found in subsequent distillation, with nevertheless, a high recovery of very high grade p-cresol. Two crystallizations and distillations should be sufficient, the first 10% and the last 4% of the distillate being discarded. For purifying m-cresol petroleum naphtha again is much superior to other solvents (mixed and otherwise); the method is the same as for p-cresol; the cooling will have to be at least to -10° C., however.

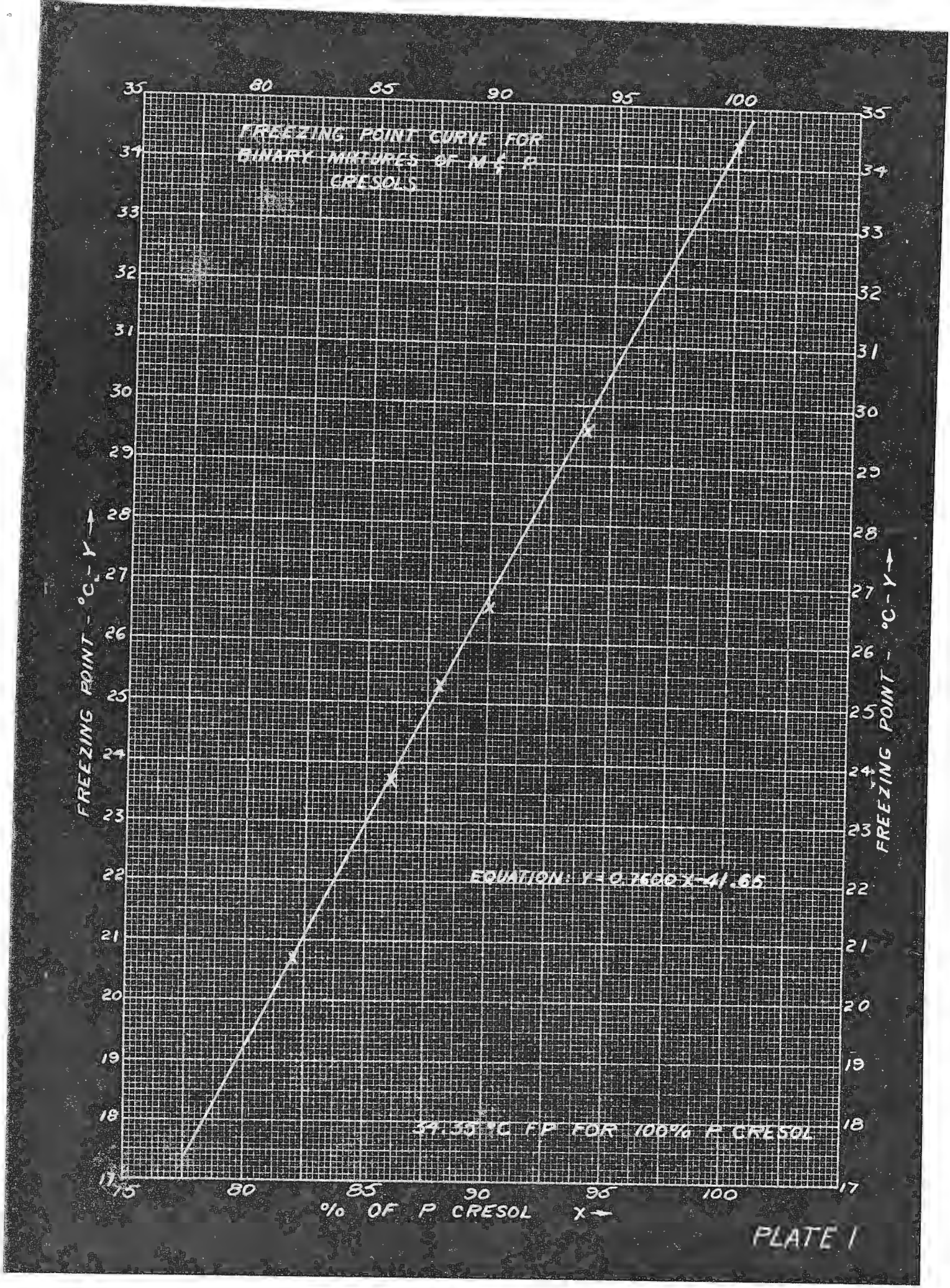
NOTE: Pure p-cresol for later freezing-point work will maintain its high freezing-point provided moisture is kept away from it. Storage in a P_2O_5 desicator is satisfactory.

APPENDIX B: Purification of Guaiacol (for Freezing-Point Work).

For the freezing-point work with guaiacol, pure guaiacol had to be prepared from some commercial material of 78% purity. This was much more difficult to do by crystallization than it had been for the cresols, but a technique was finally found which gave an excellent product in a fairly good yield (50% at poorest).

It was found that guaiacol is not soluble in petroleum ether under any conditions, but that in the other common organic solvents - toluene, alcohol, CCl_4, dioxane, ethyl acetate, propanol-2, cyclohexane, ether, and several other substances - guaiacol proved to be too soluble to come out appreciably on cooling to -10° C. or -20° C. Using a mixed solvent, with petroleum ether as one component, seemed to be the only good approach. A series of experiments were done using pte (petroleum ether) with each of the above substances and with cooling as low as -20° C. Mixtures of carbon tetrachloride, ethyl ether, toluene, and propanol-2, with pte seemed to work to some extent. The others worked poorly or not at all, as also did alcohol-water. These four successful mixtures were tested again with the conclusions that all work well (crystallization at -10° C.) but that ether and pte works best, and toluene and pte next best (and nearly as well). The procedure which was used is as follows: Enough ether is added to a 1:1 mixture of the guaiacol and pte to effect solution at approximately 5° C. At 0° to -5° C. seeding is done with guaiacol of any purity, previously frozen by dry ice, and the cooling is continued to -10° C., where a little more pte is added if no crystallization has begun. It is best that the cooling not go below -14° C.

Using this method, a 30% yield of guaiacol of 98% - 99% purity was obtained in a single crystallization from guaiacol of 78% purity. Two more crystallizations of the filtrate yielded an additional 30% of 98% material. A total recovery of 60% of guaiacol freezing from 24.3 to 25.4° C. (i.e., 97 to 98% pure) was obtained, showing the excellence of this method, inasmuch as 20 or 22% of impurities similar to guaiacol were present in the original sample.


FREEZING POINT CURVE FOR
BINARY MIXTURES OF M & P
CRESOLS
EQUATION: Y = 0.7600 X - 41.65
34.35 °C F.P FOR 100% P CRESOL
FREEZING POINT - °C - Y
% OF P CRESOL X
PLATE I