Issued July 17, 1908.

U. S. DEPARTMENT OF AGRICULTURE,

BUREAU OF ANIMAL INDUSTRY.—BULLETIN 107.

A. D. MELVIN, CHIEF OF BUREAU.

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# THE ANALYSIS OF COAL-TAR CREOSOTE AND CRESYLIC ACID SHEEP DIPS.



BY

ROBERT M. CHAPIN,
*Assistant Chemist, Biochemic Division.*



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# LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Animal Industry,
*Washington, D. C., April 13, 1908.*

Sir: I have the honor to transmit herewith and to recommend for publication as a bulletin of this Bureau the accompanying manuscript entitled "The Analysis of Coal-tar Creosote and Cresylic Acid Sheep Dips," by Robert M. Chapin, assistant chemist in the Biochemic Division.

The Department, in accordance with Bureau of Animal Industry Order 143, sanctions the use of certain classes of preparations for the official dipping of sheep and cattle. A large number of dips are manufactured and used throughout the country, and samples are constantly being submitted to the Department for the purpose of having their use permitted in official dipping, the analytical work as a basis for passing on them being performed in the Biochemic Division of this Bureau.

This paper deals with methods of determining the various constituents of dips prepared from coal-tar derivatives. It has become of some importance to find methods of analysis which shall be sufficiently accurate and at the same time not make excessive demands upon the skill or time of the analyst, and the methods proposed in the paper appear to be comparatively simple and considerably more accurate than those heretofore employed. They should accordingly be useful to persons concerned in the examination and production of such dips, and are expected to assist manufacturers in meeting the Department's requirements.

Respectfully,

A. D. Melvin,
*Chief of Bureau.*

Hon. James Wilson,
*Secretary of Agriculture.*

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## INTRODUCTORY.

The Department of Agriculture at present sanctions the use of properly constituted coal-tar creosote and cresylic acid preparations, commonly termed "dips," for the official dipping of sheep for the cure of scabies. The proprietor of each dip must, however, fulfill certain requirements in order that the use of his product may be permitted in official dipping, involving the submission of a sample to the Department for examination.[a] The Biochemic Division of the Bureau of Animal Industry has accordingly been obliged to examine a large number of these compounds and to confront the problem of finding analytical methods of considerable accuracy which would yet not make excessive demands upon the skill or time of the analyst. While these substances have, of course, afforded a field for investigation by a number of different workers, so far as known no other laboratory has been compelled to make their detailed examination such a matter of routine. Accordingly the methods here applied may be of interest to others who have occasion to examine these or similar compounds, as well as to manufacturers.

## COAL-TAR CREOSOTE DIPS.

These dips are quite simply made by dissolving rosin in phenol-bearing coal-tar oils, adding an aqueous solution of caustic soda and applying a moderate degree of heat until saponification is complete. The undiluted dip should be a clear, uniform liquid, showing no separation of its constituents. When properly diluted with a considerable quantity of water there results a permanent, uniform emulsion, from which, on standing, no oily layer or globules should separate either at top or bottom.

The completed dip will contain, then, the following substances: (1) Coal-tar hydrocarbons, (2) phenols, (3) pyridin and other volatile bases contained in coal-tar oils, (4) rosin acids, (5) soda ($Na_2O$), (6) water. In special cases certain other substances may be looked for. The rosin acids and soda will be present in approximately

[a] Bureau of Animal Industry Order 143.

equivalent proportions in combination as a rosin soap. To the latter substance is due the power of the dip to form a perfect emulsion when diluted with water.

### CURRENT METHODS OF ANALYSIS.

Methods of analysis heretofore employed may be classified into (*a*) commercial and (*b*) scientific.

The commercial methods aim at quick results and assume that the hydrocarbons and phenols alone need be determined, since they are the essential ingredients of the dip. A measured or weighed amount is shaken with aqueous sulphuric acid, the separated aqueous layer is run off, and the residual oily portion is poured into a fractionating flask and distilled into a graduated cylinder until rosin begins to decompose, as shown by the character of the vapors and the distillate. The distillate will then supposedly contain all the phenols and all the coal-tar hydrocarbons except a slight amount remaining in the flask, which, however, is in a measure balanced by a small amount of rosin oil in the distillate. After taking the volume and specific gravity of the distillate in the cylinder, strong aqueous caustic soda is introduced; the cylinder is then stoppered and thoroughly shaken. Phenols will be taken up by the caustic soda, and will be contained in the alkaline aqueous layer which separates after the cylinder has stood some time. The volume of hydrocarbons in the amount of dip taken may then be read directly, and the volume of phenols may be obtained by difference or by noting the increase in volume of the soda solution.

The process undoubtedly undergoes some modifications in the hands of different workers, but the foregoing is a general outline of a class of methods which are apparently used considerably by commercial chemists, judging from information which has come to the Biochemic Division from several different sources.

The scientific methods follow in general the system given by Allen.[a] Fifty grams of dip are shaken with ether and aqueous sulphuric acid. Bases are removed in the aqueous layer, which is then treated with excess of sodium hydroxid, and the volatile bases are distilled off with steam and determined in the distillate by titration with standard acid and methyl orange. The ethereal portion is shaken with aqueous caustic soda, which removes phenols and rosin acids, leaving in ethereal solution hydrocarbons which are weighed after expulsion of ether. The alkaline aqueous solution of phenols and rosin acids is acidified with sulphuric acid, and the phenols are distilled over with steam and determined in the distillate by any suitable method. The distillation flask containing the rosin acids is

[a] Allen, A. H., Commercial Organic Analysis, 3d ed., Vol. II, Pt. II, p. 262. 1901.

cooled, the rosin acids are separated by ether and, after expulsion of ether, weighed. Soda is determined by ignition of a small portion of the dip in a crucible, either to sodium carbonate or, with addition of sulphuric acid, to sodium sulphate.

### CRITICISM OF METHODS.

The commercial method of analysis, while rapid, contains some serious sources of error. Obviously a little of the phenols is lost in the acid aqueous extract. Moreover, practically all dips contain more or less voluminous insoluble carbonaceous matter, which conduces to the formation of an emulsion at the junction of the two layers in the separating funnel. Loss of hydrocarbons and phenols results if this emulsion is run off, while if allowed to remain with the oily layer, water together with sulphur dioxid or hydrogen sulphid will pass into the distillate, all of which tend to increase unduly the volume of hydrocarbons and phenols when the latter are measured. It is also difficult to decide exactly when to stop distillation, particularly in those dips containing oils of very high boiling point. In any case the distillate will contain some rosin oil, while some coal-tar oil will be left behind with the rosin, the relative amounts of which will vary according to the individual judgment of the analyst and will depend to a considerable extent upon the character and proportions of rosin and coal-tar oil in the particular dip under examination.

But the most serious source of error, and the one which by itself renders the method utterly untrustworthy, is the fact that undecomposed rosin is distilled along with the hydrocarbons and phenols. This rosin, which in dips containing much oil of high boiling point may amount to several grams, is of course taken up by the aqueous caustic soda with which the distillate is shaken, and will consequently cause the amount of phenols to appear several per cent too high. Nor is the presence of rosin in the distillate due to carrying the distillation too far. To decide this point dips were distilled as described, and the distillate was collected in six to eight fractions. Each fraction was treated according to the scientific method for the separation of hydrocarbons, phenols, and rosin. The results showed that rosin began to come over soon after 200° C. had been reached, and continued to appear in increasing quantity, while the distillation of phenols is certainly not complete at 250° C. It appears, therefore, utterly useless to attempt to develop any accurate method of analysis along these lines.

The scientific method, though far superior to the commercial in accuracy, possesses many disadvantages. As is well known, hydrocarbons are considerably soluble in aqueous sodium resinate and sodium cresylate, while both of these latter salts, particularly cresy-

lates, are readily hydrolyzed, and yield notable amounts of their acids to ether. Hence many extractions and reextractions are necessary to obtain anything like a complete separation of hydrocarbons from rosin and phenols, and the process requires much time and much ether. Moreover, it is often impossible to obtain a satisfactory result on weighing the hydrocarbons because their volatility renders it difficult to free them completely from ether and moisture without undue loss. Many dips contain a certain percentage of light oils, and obviously results may then be far from the truth. Petroleum ether, with the accompanied use of alcohol, offers no advantages in the operation of extraction, and renders the final weight of hydrocarbons still more uncertain.

### METHODS OF ANALYSIS ADOPTED BY THE BUREAU.

In deciding upon an official method of analysis it was desirable to adopt one that would not depend largely upon the individual judgment of the analyst, but would give definite and concordant results when the same sample was handled by different operators, and these results should closely approximate the truth. It is evident that the scientific method just referred to is far from satisfactory in this respect. It is also evident that no method which involves separation of the hydrocarbons and the determination of their weight can yield results free from suspicion. For the other ingredients of these dips workable methods have been found which attain reasonable accuracy and give concordant results in the hands of any chemist of ordinary ability with a little practice, and which do not make excessive demands upon time nor require expensive chemicals. It has seemed best, therefore, to determine these other ingredients, to subtract the total of the percentages so obtained from 100, and to call the remainder "hydrocarbons."

The following methods are accordingly those now employed in the laboratories of the Biochemic Division. The dip is well shaken before weighing, and the latter operation is most conveniently performed by pouring into a beaker somewhat more than the amount needed, balancing on the scales, and pouring off the desired amount into the receptacle to be used in the analysis.

### DETERMINATION OF WATER.

Fifty grams of dip is weighed into a 100 c. c. fractionating flask with a moderately high side tube, beyond the exit of which the neck should continue for not more than one inch, and the flask is connected with a small water-cooled condenser and carefully heated with a smoky flame until oils come over freely and carry no trace of water with them, but the distillation should not be unnecessarily continued.

The distillate is received in a properly graduated 25 c. c. cylinder, allowed some time to separate completely, and the volume of water read. The number of cubic centimeters of water multiplied by 2 equals the percentage of water. Ordinarily the process offers no difficulties. A dip extremely high in rosin may bump and froth over, no matter how carefully heated. In such a case a larger flask is used, and the dip is diluted with about an equal volume of water-free mineral or coal-tar oil. In case separation of the distillate is imperfect a small measured amount of strong NaCl solution is added from a pipette, and the cylinder is nearly filled with benzol, shaken, and left at rest for some time. The volume of NaCl solution added is of course to be deducted when the reading is taken.

DETERMINATION OF SODA AND PYRIDIN BASES.

The method, which is a novel combination and adaptation of well-known principles and processes, depends upon the fact that pyridin bases are alkaline toward methyl orange, but not toward phenolphthalein. A known weight of dip is shaken in a separatory funnel with ether and water to which a known amount of sulphuric acid has been added. Rosin soap is thus decomposed, and all bases contained in the dip will pass as sulphates into the lower acid aqueous layer which soon separates. The latter is quantitatively removed, and, ignoring acid salts for the sake of simplicity, will contain the substances—

| | (a) | (b) | (c) |
|---|---|---|---|
| Stage I. | $Na_2SO_4$. | $H_2SO_4$. | $(C_5H_5N)_2H_2SO_4$. |

If methyl orange is now added and the solution titrated to neutrality with standard caustic soda the result will be—

| | (a) | (b) | (c) |
|---|---|---|---|
| Stage II. | $Na_2SO_4$. | $Na_2SO_4$. | $(C_5H_5N)_2H_2SO_4$. |

If next phenolphthalein is added and titration with standard caustic soda continued until the solution is neutral to that indicator, the final condition of the solution will be—

| | (a) | (b) | (c) | |
|---|---|---|---|---|
| Stage III. | $Na_2SO_4$. | $Na_2SO_4$. | $Na_2SO_4$. | $C_5H_5N$. |

Obviously the amount of caustic soda required to change the solution from Stage II to Stage III will be a measure of the amount of pyridin present, while if the amount of caustic soda added in the whole titration is subtracted from the equivalent in soda of the sulphuric acid originally introduced the remainder will equal the amount of soda in the dip. Briefly, the amount of soda equivalent to $H_2SO_4$ (c) measures pyridin; soda equivalent to $H_2SO_4$ [(a+b+c)—

(b+c)] is the soda of the dip. The process is executed in the following manner:

Ten grams of dip is weighed into a 200 c. c. short-stemmed separating funnel, 50 c. c. ether added, exactly 30 c. c. of N/2 $H_2SO_4$ run in from a burette and the funnel shaken. The lower aqueous layer, which now contains the bases, is drawn off completely, together with any insoluble carbonaceous matter which may appear at the junction of the two layers. No harm is done if a small amount of the ethereal layer accompanies the insoluble matter in the separation. The ethereal solution remaining in the funnel is next washed four times with water, using about 20 c. c. each time. In the first of these washings the funnel should not be shaken, but the water should be drawn off at once, the object being to wash out the stem of the funnel and so avoid loss of a little acid therein contained.

All the aqueous extracts are united and heated on the steam bath for expulsion of ether. The liquid is then passed through a wet filter into a 300 c. c. flask, the filter washed with hot water, the flask cooled, filled to the mark, and the contents exactly divided between two uniform titrating flasks of about 300 c. c. capacity. To one of these portions add methyl orange, then N/2 NaOH till the red tint just disappears, as nearly as can be determined by comparison with the second portion. Then add one-tenth or two-tenths of a cubic centimeter more of N/2 NaOH to make sure that neutrality has been reached, though much excess must be avoided, else the separation of higher pyridin bases will render the solution turbid.

This first titration is not quantitative, but merely to afford a standard of comparison, by the aid of which the second portion is quantitatively titrated to exact neutrality, after the addition of an equal amount of methyl orange. The number of cubic centimeters of N/2 NaOH used is noted, phenolphthalein added, and the titration continued to the end point of that indicator. To obtain the per cent of $Na_2O$ in the dip, subtract the total number of cubic centimeters of N/2 NaOH used in the whole titration of the second portion from 15, and multiply the remainder by 0.31. To obtain the per cent of volatile bases reckoned as pyridin, multiply the number of cubic centimeters of N/2 NaOH used between the end points of methyl orange and phenolphthalein by 0.79. The only difficulty in the method is the determination of the point of neutrality toward methyl orange, but a proper use of the standard of comparison will satisfactorily overcome this.[a]

[a] Recent work has indicated that the coloring matters which tend to interfere with the accurate observation of the end point with methyl orange may be almost entirely removed from the solution by the use of animal charcoal. Powdered animal charcoal is digested on the steam bath with dilute hydrochloric acid in sufficient quantity to decompose and dissolve all carbonates and

Results obtained for pyridin run between 0.05 and 0.1 per cent higher than by Allen's method.

### DETERMINATION OF PHENOLS.

The regulations of the Department of Agriculture [a] include under the designations "phenols," "cresols," and "cresylic acid" those phenols whose boiling points range between 185° C. and 250° C. Benzophenol, or pure carbolic acid, having a boiling point of 182° C., is accordingly excluded, the reason for such distinction being that it is considerably more toxic in its effect upon animals than the phenols of higher boiling points. As a matter of fact the comparatively high market value of pure carbolic acid as a separate product renders unlikely the presence of more than traces of it in such compounds. It is well known that the so-called crude carbolic acid of commerce consists almost entirely of higher phenols.

There are but few methods for determining phenols which have received at all extended application. Of these the only direct acidimetric method, that of Bader,[b] is applicable to benzophenol alone, and hence is of no value in the present case. A direct gravimetric determination, in addition to its inherent sources of error, demands a complete separation of hydrocarbons from the phenols. So also does any volumetric method based upon the reaction between phenols and bromin or iodin. This separation of hydrocarbons from phenols, as noted under the description of the scientific method of analysis, is tedious and uncertain, and is to be avoided if in any way possible.

There will appear, then, to be two methods practically applicable in the present case—the method of Schryver,[c] by which the phenols are acted upon in benzol solution by sodamid and the evolved ammonia titrated, and the German method of measuring the increase in

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phosphates present, then washed with hot water until the wash water is free from chlorids, and finally dried and powdered.

In the course of an analysis, after the flask containing the acid extract from the dip has been heated upon the steam bath until ether has been completely expelled, 1 to 1.5 grams of the purified animal charcoal is added, and the flask, frequently shaken, is left upon the steam bath for 30 to 60 minutes. The contents are then filtered, washed, and titrated as usual. After proper treatment with animal charcoal in this manner the solution will be a pale green in color, possessing none of the muddy yellow tint which tends to obscure the end point with methyl orange.

Experiments have thus far failed to show that any inaccuracy is introduced into the method by the use of animal charcoal in the manner described.

[a] Bureau of Animal Industry Order 143, p. 18.

[b] Zeitschrift für Analytische Chemie, Jahrg. 31, p. 58–60. Wiesbaden, 1892.

[c] Journal of the Society of Chemical Industry, vol. 18, No. 6, p. 553–556. London, June 30, 1899.

volume of a caustic soda solution when the phenols are absorbed by it. In either case the phenols may be separated from interfering substances by steam distillation of the acidified dip. Schryver's method is essentially a direct determination of the amount of phenol hydroxyl present, and the actual weight must be obtained through a knowledge of the mean molecular weight derived from other considerations. The German method, on the other hand, is a measure of the volume of the phenols when in solution under certain conditions, and the corresponding weight can be obtained only by the employment of an empirical factor or coefficient found to hold true for that particular kind of phenol under those particular conditions. Since in both methods a certain factor must be somewhat arbitrarily adopted by which the numbers directly obtained are to be multiplied in order to obtain the weight of phenols present, and since the possible error thereby involved appears of about the same magnitude in both, that one will naturally be chosen which is easiest of execution, in which respect Schryver's method is at a decided disadvantage.

The methods of procedure which considerable experimental work has shown to be satisfactory is as follows:

Fifty grams of dip is weighed into a 500 c. c. round-bottomed flask, 20 c. c. of 1:3 $H_2SO_4$ is added, and the phenols are distilled off with steam. The flask will require no heating if a rapid current of steam is passed into it, but may with advantage be packed in cotton or felt. Obviously the apparatus must be so set up and the distillation so conducted that particles of rosin may not be mechanically carried over by the current of steam. Toward the end of the distillation any naphthalene in the condenser is melted out by shutting off the water for a few minutes, or if separated earlier in sufficient quantity to threaten stoppage of the condenser tube, distillation is interrupted while hot water is run through the condenser. The distillate is received in a liter flask approximately marked for each 100 c. c. capacity and joined to the condenser by a cork which is pierced by a small glass tube connected to a small U tube containing a little dilute caustic soda. The latter acts as a trap to prevent any loss of the distilled phenols. Distillation is continued until 1 or 2 c. c. collected in a test tube gives no reaction with any appropriate reagent for phenols, such as ferric chlorid. A volume of 800 c. c. is ample in nearly all cases.

A supply of benzol should be prepared by shaking a good grade of benzol with dilute sulphuric acid, then with dilute caustic soda two or three times, and then passing through a dry filter. A small wash bottle containing some of this benzol will be found very useful for rinsing the necks of separatory funnels, etc. Of this purified benzol 150 c. c. is measured out conveniently at hand, the contents of

the U tube and 5 c. c. of 1:1 $H_2SO_4$ are added to the distillate, and the latter is shaken up and poured into a separatory funnel of 1,500 c. c. capacity, the flask being rinsed out with successive portions of the 150 c. c. benzol. When all is in the funnel 25 grams of clean sodium chlorid is added for each 100 c. c. of distillate, and the funnel is well shaken for five minutes and left at rest one-half hour. The aqueous layer is then run off slowly and completely, the funnel being allowed to stand until there is no further separation. The benzol solution of phenols and hydrocarbons is transferred to a 500 c. c. Erlenmeyer flask, while the aqueous portion is poured back into the separating funnel and extracted twice more in the same way, 100 c. c. of benzol being used each time. The funnel should always be gently handled after the aqueous portion has been drawn off, to prevent any impurities from the sodium chlorid which have deposited upon its sides from becoming mixed with the benzol solution. The three benzol extracts are united in the Erlenmeyer flask, 15 c. c. of pure caustic soda solution, 1:2, is added, and the contents of the flask are subjected to a rotatory motion for some time in order that the phenols may be taken up by the caustic soda as completely as possible.

After the addition of a few grains of sand the flask is immersed in a water bath, connected to a condenser, and all but 40 to 50 c. c. of the benzol distilled off. With the aid of a wash bottle containing water and provided with a fine jet, only a small portion of water being used at a time, the contents of the flask are next carefully washed into a 150 c. c. separatory funnel. With proper manipulation the flask should be completely washed when the volume of aqueous portion in the separatory funnel amounts to not more than 50 c. c. Ten cubic centimeters of strong sulphuric acid (100 c. c. pure concentrated $H_2SO_4$ to 120 c. c. water) is next slowly introduced with gentle rotation of the funnel, the addition of acid being interrupted and the funnel cooled whenever it becomes unpleasantly warm to the hand. Two or three drops of methyl orange are now added; and if on mixing the contents of the funnel the lower layer does not acquire a pink color, the addition of acid is continued until acidity is assured. Sufficient benzol is then added to make the two layers in the funnel approximately equal in volume, the funnel is thoroughly shaken and, with loosened stopper, left at rest for two hours. After that time the aqueous layer is slowly and completely run out, the analyst making sure that on longer standing no more will drain down from the sides of the funnel. The benzol solution of phenols is then ready to be transferred to the measuring tube.

The measuring tube consists of a glass-stoppered pear-shaped bulb of about 100 c. c. capacity, joined at its tapering end to a tube about 1 foot long and of a capacity of 25 to 30 c. c. This tube is accurately

graduated to contain 25 c. c. at 20° C. in divisions of one-tenth c. c. (See fig. 1.)

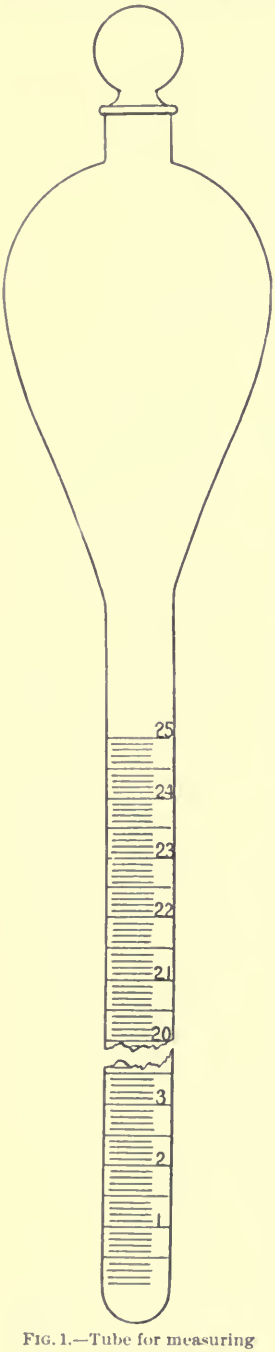


FIG. 1.—Tube for measuring phenols.

The apparatus is cleaned thoroughly with soap powder and hot water, and dried, best spontaneously, though alcohol and ether may be used if pure. Perfect cleanliness is essential to insure a properly shaped meniscus. Between 15 and 16 c. c. of caustic soda solution, 1:3, is brought into the tube with a pipette. The caustic soda should not be allowed to come in contact with the interior of the bulb or the upper part of the tube. After a few moments about 1 c. c. of benzol is added, and after waiting a little the height to the top of the now almost flat meniscus is noted. The benzol solution of phenols is next transferred from the separatory funnel to the tube, care being used to avoid mixing with the soda; the separatory funnel is washed out with a little benzol, which is also transferred to the tube, and the height of the meniscus is again noted. The latter may often be obtained more accurately at this point. The tube is then stoppered, vigorously shaken for three minutes, and set aside for at least three hours. An occasional rapid rotation of the tube between the palms of the hands will insure a complete separation of the layers. Each cubic centimeter increase in volume of the caustic soda solution may be taken to represent one gram of phenols. All readings of the tube should be taken at the top of the meniscus and at a temperature as near 20° C. as practicable.

This method of treating the distilled phenols is essentially that of Spalteholz,[a] though the details of its execution were not imparted in the original communication and had to be worked out independently. A discussion of the reasons for the different steps of the foregoing process will be entered into in a later section which deals with the experimental work done (see page 27).

[a] Chemiker-Zeitung, jahrg. 22, no. 8, pp. 58–59, Cöthen, Jan. 26, 1898.

From certain experiments it seems possible that a continuous extraction apparatus may be successfully employed to extract phenols from the aqueous distillate of the dip, using benzol as the solvent, and introducing caustic soda solution into the distillation flask of the apparatus at the beginning of the operation to retain the extracted phenols. When the extraction is completed the small flask of the apparatus will contain all the phenols, dissolved in a limited amount of caustic soda solution and overlaid by about 50 c. c. of benzol. The contents of the flask may then be brought readily and completely into a separatory funnel and acidified in the usual manner. Certain exigencies of the work in this laboratory have rendered somewhat inconvenient at the present time a practical test of this method of procedure in the routine examination of dips submitted for analysis.

### DETERMINATION OF ROSIN ACIDS.

Resins in general have been shown to contain at least three different classes of bodies:[a] (1) resin acids or anhydrids, (2) esters of these or similar acids, (3) indifferent neutral bodies, perhaps hydrocarbons. Common rosin, or colophony, contains, according to Allen,[b] between 83.4 and 93.8 per cent of free rosin acids or anhydrids. The remaining 6 to 17 per cent consists of neutral bodies, soluble in ether and not extracted from ethereal solution by aqueous caustic soda, and accordingly there would seem to be no practicable means of distinguishing and separating them from the coal-tar hydrocarbons of the dip. Apparently, then, the analyst must be content with a determination of the amount of rosin acids present, which will represent about nine-tenths of the amount of rosin actually used in manufacturing the dip. Either a gravimetric or a volumetric method may be employed.

Owing to the degree of uncertainty attached to the exact combining equivalent of the rosin acids in each particular dip, the gravimetric method has an indubitable advantage in point of accuracy when properly carried out. But as a matter of fact the combining equivalents of a considerable number of rosin acids obtained from different dips in the gravimetric way in the course of analysis have been found to vary very little, not enough in any case to cause a possible error of half a per cent in the analysis of a dip of ordinary constitution. Moreover, in view of the difficulty of completely separating hydrocarbons from rosin acids, as is necessary in the gravimetric method, it is probable that the ordinary analyst without considerable practice in this particular operation will obtain quite as accurate results by the volumetric method as by the gravimetric. Accordingly the

[a] Allen, A. H., Commercial Organic Analysis, 3d ed. rev., Vol. II, Pt. III, p. 141. 1907.

[b] Id., p. 160.

volumetric method would seem to recommend itself for use in ordinary routine work on account of its greater rapidity, simplicity, and probable equal accuracy under ordinary conditions, while the gravimetric method may be reserved for dips extremely high in rosin or for a confirmatory method in special cases.

For the determination of rosin acids by either method it is most advantageous to make use of the residue left in the distillation flask after the determination of phenols. From this residue all phenols and a large part of the hydrocarbons have been removed, hence the necessary extraction by ether is expedited. After cooling, the aqueous portion of the contents of the flask is poured into a separatory funnel, with as little rosin as possible, and extracted with ether. The aqueous portion is run off and discarded, the residue in the flask is completely dissolved and brought into the funnel with ether, 40 to 50 c. c. of water is added, and the funnel well shaken. The presence of insoluble carbonaceous matter will usually cause a persistent emulsion at the junction of the two layers, which may, in fact, entirely fill the lower part of the funnel.

This is wholly run off into a 300 c. c. Erlenmeyer flask and the ethereal solution well shaken again with successive portions of water, the water being run off each time to the clear ethereal solution, until the carbonaceous matter is wholly removed and separation takes place in the funnel quickly and cleanly. These wash waters are all received in the flask containing the first separated emulsion, and this is heated upon the steam bath until ether is expelled. The contents are then brought more or less completely upon a wet filter and washed with hot water. At this point the methods diverge.

*Gravimetric method.*—In case the gravimetric method is to be employed, after a brief washing of the insoluble carbonaceous residue with hot water both flask and filter are well drained. Both are then washed, first with a little absolute alcohol to remove water, then thoroughly with ether until all rosin is dissolved and the filtrate comes through colorless.

The united ethereal solution of hydrocarbons and rosin is now thoroughly shaken with about 40 c. c. of 15 per cent caustic soda. On separation there will be three layers. The lowest one usually contains very little rosin soap, and consequently holds but a small amount of hydrocarbons. It is best run off and washed separately with ether. One washing will usually free it completely from hydrocarbons.

After the first layer has been thus removed, about 50 c. c. of water is added to the funnel and the latter is well shaken. The lower layer of rosin soap is run off and followed by 5 to 10 c. c. of water without shaking, the funnel being given only a gentle rotatory motion. The remaining ether solution of hydrocarbons is washed twice with 20

to 25 c. c. of about 4 per cent caustic soda solution, each washing being followed by a little water as before described. These two washings with dilute caustic soda are kept apart and not added to the main solution of rosin soap.

The main solution of rosin soap is now washed in a separatory funnel with successive portions of ether, followed through each time by 5 c. c. of water, as at first, until the ether is left nearly colorless. The ether extracts are shaken through in their order with the two washings of dilute caustic soda already used, and a third if needed, each being followed with a few cubic centimeters of water.

All the aqueous extracts are united in a porcelain dish or casserole, which should be not more than half filled by them, and are evaporated on the steam bath until ether is dissipated and the volume reduced to a convenient amount. The contents of the dish are then transferred to a separatory funnel with the aid of a spatula and hot water; strong sulphuric acid is added to decompose all rosin soap, and after complete cooling the rosin acids are extracted by ether and washed with water till free from sulphuric acid. The ethereal solution is brought into a weighed Erlenmeyer flask with a few grains of sand, the ether is distilled off, and the flask is heated in an oven at 110° C. until the absence of frothing on rotation shows elimination of water; it is then cooled and weighed.

*Volumetric method.*—As already noted, the volumetric method proceeds identically with the gravimetric to the point where carbonaceous matter is brought upon the filter and washed with hot water. The washing in this case must be continued until the wash water comes through entirely free from acid reaction. The main ethereal solution has meanwhile been brought into a flask and the ether distilled off. The filter funnel is set in the neck of this flask, and the carbonaceous matter is washed with hot alcohol previously rendered neutral to phenolphthalein, until freed from rosin. The alcoholic solution of rosin is brought into a graduated flask, and an aliquot part, usually one-fourth, taken for titration with half-normal caustic soda. The titration is conveniently carried out in a 200 c. c. Erlenmeyer flask in a volume of 100 to 125 c. c., the portion taken being diluted with neutralized alcohol to that amount.

Owing to the very dark color of the liquid an external indicator is necessary. For this purpose alkali blue is best adapted. A few drops of a strong alcoholic stock solution are added to 25 or 30 c. c. of alcohol, which is then carefully neutralized with tenth-normal caustic soda. Enough alkali blue should be added to produce a deep color, almost a cherry, when neutralized, with no trace of violet. This dilute indicator should be freshly prepared. A supply of small test tubes 8 to 10 millimeters in diameter and 60 to 80 millimeters long should be at hand, cleaned and dried. When a test of the progress

of the titration is to be made about ½ c. c. of prepared indicator is poured into one of these test tubes, and to this is added a drop of the liquid under titration. If a violet color appears, the solution still contains free rosin acid, and more N/2 NaOH must be added and the solution again tested with a fresh tube of indicator. If the indicator does not show a violet color upon the addition of one drop of the liquid under titration, addition of the latter is continued drop by drop until an amount has been added approximately equal in volume to the amount of indicator originally in the tube, i. e., ½ c. c. The continued absence of a violet color after the addition of this amount indicates that the solution is either neutral or alkaline. The end of the titration then is reached when a greenish or violet tint just fails to appear. A fresh tube of indicator must be used for each test. It is best to proceed by running in 12 to 15 c. c. of half-normal caustic soda at once, testing and continuing addition if necessary, a cubic centimeter at a time, until the indicator shows alkalinity, then running back with half-normal hydrochloric acid, using perhaps 0.4 c. c. at a time till acidity is shown, and now working carefully with half-normal caustic soda to exact neutrality. One cubic centimeter of half-normal caustic soda is considered to be equivalent to 0.162 gram of rosin acids.

Phenolphthalein may also be used as an indicator in a similar way, by preparing an alcoholic solution of quite a deep rose tint. The end point of the titration will then be reached when the indicator, used in the same way as alkali blue, is no longer bleached by the addition of the liquid under titration. The color change is not so marked as in the case of alkali blue, and consequently the end point is not so sharp, though almost equally good results may be obtained with a little care and practice.

All alcoholic solutions should be kept from contact with air as far as possible to prevent absorption of carbon dioxid.

### DETERMINATION OF OCCASIONAL INGREDIENTS.

*Light oils.*—The presence of light oils will usually be indicated by the relative proportions of oil and water which come over in the early stages of the process of distilling the dip for the determination of water. The odor of the distillate should be noted at this point, to identify if possible the nature of the light oils present. If more information is desired, about 150 grams of dip is thoroughly shaken with 20 to 25 c. c. of 1 : 3 sulphuric acid, allowed some hours to separate, and a weight of oils, etc., equivalent to 100 grams of dip—i. e., a weight in grams equal to the sum of the percentages of hydrocarbons, phenols, and rosin—is distilled from an Engel flask fitted with a thermometer until the temperature reaches 180° C. The distillate is measured and further examined in any way desired.

*Naphthalene.*—Too large a proportion of naphthalene or other solid hydrocarbons is undesirable on account of the liability of these bodies to separate from the dip in freezing weather and remain for a long time as an undissolved sediment. For an approximate determination of the amount of solid hydrocarbons present 50 grams of dip is acidified with a little concentrated hydrochloric acid, 100 c. c. alcohol added, and the containing vessel immersed in a freezing mixture for two hours, with occasional stirring. The separated hydrocarbons are then filtered off on a Buchner funnel or plate, washed somewhat with chilled alcohol, well drained, and pressed out in a letterpress between several thicknesses of filter paper. The mass may then be weighed and subjected to any further examination desired. A more practical test is to subject a portion of the dip itself to a temperature of 0° C. for about three hours, with occasional shaking or stirring. It should remain perfectly clear and liquid and show no separation of solid matter.

*Foreign oils and creosotes.*—By the regulations of the Secretary of Agriculture[a] the degree of dilution which may be accorded to a coal-tar creosote dip is explicitly made to depend upon the percentages of coal-tar oils and cresylic acid contained in the dip. Accordingly in the standardization of dips for official use, within the scope of the regulations, petroleum oil, rosin oil, or creosotes of other origin than coal-tar must be regarded as extraneous substances. Investigations are now in progress to find satisfactory methods for detecting and estimating these substances when present in dips. At the present time, however, this line of work has not reached a point of development which warrants the publication of any results.

## CRESYLIC ACID DIPS.

Cresylic acid or cresol dips in composition approximate more or less closely the "liquor cresolis compositus" of the United States Pharmacopœia, eighth revision, 1905, being made from a potash-linseed oil soap and cresylic acid comparatively free from hydrocarbons. A properly prepared dip of this character should upon dilution in 100 parts of distilled water yield a practically water-clear solution, showing absence of any notable amount of hydrocarbons or unsaponified oil. On dilution, however, with hard water there will naturally be some turbidity, caused by the precipitation of soap. A portion of the dip when treated with successive small portions of water should show itself miscible in all proportions. At no stage should there be any notable turbidity or separation of heavy oily globules of cresylic acid due to absence of sufficient soap.

[a] Bureau of Animal Industry Order 143, p. 18.

### METHODS OF ANALYSIS ADOPTED BY THE BUREAU.

The methods of analysis adopted are essentially the same as for coal-tar creosote dips, modified in details to suit the somewhat different composition of the substances.

#### DETERMINATION OF WATER.

The distillate must always be received in a stoppered cylinder and treated with benzol and sodium chlorid solution as described. The results will be about 0.5 per cent too low. The addition of toluene or a similar hydrocarbon to the dip before distillation might possibly improve the results.

#### DETERMINATION OF POTASH (OR SODA) AND PYRIDIN.

A preliminary test is here necessary to determine whether potash or soda is the alkali present. The test may be conveniently made by shaking about 10 grams of dip with ether and a little dilute hydrochloric acid, drawing off the aqueous layer, and applying the flame test with a platinum wire, supplementing this with any other confirmatory test necessary or desirable. If potash is found to be the alkali present the factor 0.471 must be used in place of the factor 0.31 employed in the case of soda.

#### DETERMINATION OF PHENOLS.

Since the percentage of phenols will here be much higher than in coal-tar creosote dips, a smaller amount of dip must be taken for analysis, usually 15 to 20 grams. The amount should be as large as possible, in order that the greatest quantity of phenols within the capacity of the tube may be brought to measurement. A new opportunity for error is here afforded. Linseed oil possesses a low Reichert-Meissl number, 00 to 1.43.[a] This means that a small amount of volatile fatty acid will accompany the phenols through the stages of the process and tend to cause too high results. To determine the possible amount of this error 25 grams of linseed oil was saponified, then acidified, and distilled with steam until 800 c. c. had been collected. The distillate was treated by the regular method and an increase in volume between 0.02 and 0.07 c. c. observed. In view of the fact that this quantity of soap is four or five times as much as would be present in an ordinary analysis, the error which is likely to arise from this source would appear negligible.

#### DETERMINATION OF ROSIN OR FATTY ACIDS.

The odor of the dip itself, and more especially the character of the residue left in the flask after the distillation of phenols, will inform

[a] Hopkins's Oil Chemists' Handbook, page 38.

the analyst whether rosin or fatty acids are to be determined. Rosin will collect in a solid, hard button at the bottom, while fatty acids will form a liquid oily layer floating upon the surface of the aqueous contents. In either case the whole is extracted with ether, washed with water, and, after evaporation of ether, dissolved in neutralized alcohol and titrated with half-normal caustic soda. One cubic centimeter of half-normal soda will represent 0.138 gram fatty acid anhydrids[a] and 0.015344 gram glycerin. Cresol dips containing rosin soap are not at present permitted in official dipping.

Such a detailed analysis of a cresol dip would appear, however, seldom necessary. Phenols must of course be determined as accurately as possible. An examination of the odor and appearance of the residue left in the flask after distillation of phenols will indicate the character of the soap employed. If, then, the behavior of the dip upon dilution is satisfactory (page 21) and indicates the presence of sufficient soap, the only remaining question is whether there may be an unnecessary and possibly harmful amount of alkali present. In the presence of the large amount of cresylic acid contained in these dips there can be, strictly speaking, no "free alkali." The ideal cresol dip will, however, unquestionably contain no alkali above that necessary to obtain complete saponification of the linseed oil. An excess of alkali can be of no possible benefit and might conceivably be undesirable for several reasons. A useful test for the presence of such an excess of alkali is that of Kelhofer.[b]

Ten grams of dip is thoroughly shaken in a small separatory funnel with 50 c. c. of a saturated solution of NaCl. After complete separation has taken place the lower aqueous layer is removed, diluted with an equal volume of water, and a few drops of phenolphthalein added. If the dip has been made from a perfectly neutral linseed-oil soap, there will appear at most but a slight reddening of the solution, which vanishes upon the addition of a drop of half-normal acid. If more acid is required to remove the pink color, the presence of an excess of alkali is indicated. The test can not be made quantitative, for experiments have shown that only a part of the excess of alkali actually present is accounted for in this way, the remainder probably being thrown up in the form of alkali cresylate into the upper layer with the soap. It would seem, then, reasonable to demand that no dip treated as described should require more than a very few tenths of a cubic centimeter of half-normal acid to remove the pink color imparted by phenolphthalein to the sodium chlorid extract.

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[a] Lewkowitsch, J., Chemical Technology and Analysis of Oils, Fats, and Waxes, 3d ed., Vol. I, p. 334. 1904.

[b] Schweizerische Wochenschrift für Chemie und Pharmazie, jahrg. 46, No. 2, pp. 19–20. Zurich, Jan. 11, 1908.

Duyk[a] proposes a method for the determination of soap in cresol dips, according to which the soap is separated by shaking the dip with a strong sugar solution. The latter dissolves all the soap, which may be recovered by salting out with NaCl, and purified, if desired, by solution in alcohol. The method has not been tried in this laboratory.

## ANALYSIS OF COAL-TAR OILS AND COMMERCIAL CRESYLIC ACID.

Obviously it is impossible for a manufacturer to produce a dip of constant composition closely adhering to the standard he has set for himself in his original sample submitted to the Department of Agriculture for examination unless he knows exactly what goes into each lot of dip his factory turns out. The composition of coal-tar oils is subject to considerable variation; consequently it is absolutely necessary for any manufacturer who wishes to secure and retain permission for the use of his dip in official dipping to have at his disposal some means of accurately analyzing each lot of coal-tar oils he receives. He may then blend his oils, or his oils and cresylic acid, in such proportions as always to preserve uniform the composition of his dip.

The coal-tar oils to be used for dips must be examined for water, pyridin bases, and phenols.

Water will be determined exactly as in dips (page 10).

Pyridin bases will be determined exactly as in dips (page 11), but if the oils are old and highly colored it may prove advantageous to use 5 grams instead of 10.

The hope was entertained that phenols in coal-tar oils and cresylic acid might be readily and accurately estimated by dissolving a weighed amount in benzol, shaking with acidified aqueous sodium sulphate to remove water, and then shaking the separated benzol solution in the measuring tube with caustic soda; in short, by repeating exactly the last two steps of the method employed for phenols in dips. In fact, the latter was adopted for dips with considerable added satisfaction because it seemed to promise an easy solution of one of the most troublesome problems of dip making by affording such a simple means for valuing coal-tar oils, requiring no special technical training for its execution, and yet being a method strictly parallel in all respects to the method employed in analyzing the completed dip.

This hope was not realized, for it was found that some samples at any rate of creosote oils and of cresylic acid contain small amounts of acid bodies of some description, possibly phenoloids, possibly of a resinous nature, which are taken up by caustic soda, increasing its

[a] Annales de Chimie Analytique, t. 12, No. 9, pp. 345–346. Paris, Sept. 15, 1907.

volume, but which are not volatile with steam. There seems to be no way of determining these bodies in the dip, provided they are phenoloids; hence it seems necessary to define cresylic acid within the scope of the regulations as "phenols derived from coal tar, none of which boils below 185° C. nor above 250° C.," and which are completely volatile with steam at 100° C. The only resource, accordingly, is to handle the oils and cresylic acid in exactly the same way as the dips themselves are handled (page 13), by distillation of an appropriate weight of the acidified oil in a current of steam, with the subsequent extractions and measurement as described.

As might be expected, cresylic acid appears to contain a smaller per cent of these acid bodies not volatile with steam than does creosote oil. Very probably the amount is subject to considerable variation in different samples. Results on certain samples will be given in the section on experimental work (page 33).

## CALCULATION OF PROPER DILUTION OF DIPS.

### COAL-TAR CREOSOTE DIPS.

The regulations of the Secretary of Agriculture[a] state that a coal-tar creosote dip "should contain when diluted ready for use not less than 1 per cent by weight of coal-tar oils and cresylic acid. In no case should the diluted dip contain more than four-tenths of 1 per cent nor less than one-tenth of 1 per cent of cresylic acid; but when the proportion of cresylic acid falls below two-tenths of 1 per cent the coal-tar oils should be increased sufficiently to bring the total of the tar oils and the cresylic acid in the diluted dip up to 1.2 per cent by weight."

In calculating from the composition of a dip its proper dilution under this regulation three points must be borne in mind. First, the regulations demand that hydrocarbons and phenols must be present in certain minimum percentages by weight, whereas in practice a dip is always diluted by volume. Second, the regulations set two independent minimum pairs of values below which the percentages of phenols and of hydrocarbons and phenols may not fall, though they may rise above these set values within certain limits, thus allowing a considerable range in the possible composition of a dip. Third, the calculated dilution must be the greatest possible dilution which the dip under consideration can obtain under the regulations.

Three steps will then be involved in the calculation of the dilution of a coal-tar creosote dip. (1) The selection of the pair of minimum percentages of phenols and of hydrocarbons and phenols

[a] Bureau of Animal Industry Order 143, page 18.

most advantageous for that particular dip; (2) the calculation of the maximum dilution by weight which a dip of that composition can be granted under the section of the regulation most advantageous to it; (3) by employment of the specific gravity of the dip as a factor to pass from the obtained maximum dilution by weight to the maximum dilution by volume.

These data having been thus fully set forth, it hardly seems necessary to enter into the actual solution of the problem, since the matter is purely one of mathematics. It will be sufficient to state that a mathematical analysis of the above regulation will lead to the following four cases and the four corresponding rules for obtaining the maximum dilution in each case:

*Case I.*—When the percentage of phenols is less than one-twelfth of the sum of the percentages of hydrocarbons and phenols.

Rule: Multiply the percentage of phenols by 10, subtract 1 from the product, and multiply the remainder by the specific gravity of the dip.

The diluted dip will then contain 0.1 per cent phenols and over 1.2 per cent hydrocarbons and phenols.

*Case II.*—When the percentage of phenols is between one-twelfth and one-sixth of the sum of the percentages of hydrocarbons and phenols.

Rule: Divide the sum of the percentages of hydrocarbons and phenols by 1.2, subtract 1 from the quotient, and multiply the remainder by the specific gravity of the dip.

The diluted dip will then contain 1.2 per cent of hydrocarbons and phenols and between 0.1 and 0.2 per cent of phenols.

*Case III.*—When the percentage of phenols is between one-sixth and one-fifth of the sum of the percentages of hydrocarbons and phenols.

Rule: Multiply the percentage of phenols by 5, subtract 1 from the product, and multiply the remainder by the specific gravity of the dip.

The diluted dip will then contain 0.2 per cent phenols and between 1 and 1.2 per cent hydrocarbons and phenols.

*Case IV.*—When the percentage of phenols is between one-fifth and two-fifths of the sum of the percentages of hydrocarbons and phenols.

Rule: Subtract 1 from the sum of the percentages of hydrocarbons and phenols, and multiply the remainder by the specific gravity of the dip.

The diluted dip will then contain 1 per cent hydrocarbons and phenols and between 0.2 per cent and 0.4 per cent of phenols.

In each case the result obtained by the rule is the number of parts by volume which may be added to one part by volume of the dip; in

practice, the greatest number of gallons of water which may be added to one gallon of dip.

It may be stated that if the percentage of phenols is greater than two-fifths of the sum of the percentages of hydrocarbons and phenols, the use of the dip can not be permitted under the regulations, for when diluted until it contains 1 per cent of hydrocarbons plus phenols, the minimum allowed, it will necessarily contain above 0.4 per cent of phenols, which amount is set as the maximum limit.

### CRESYLIC-ACID DIPS.

The aforementioned regulations state in regard to the cresol dip that "when diluted ready for use this dip should contain one-half of 1 per cent of cresylic acid." From this may be derived the rule: Multiply the percentage of phenols by 2, subtract 1 from the product, and multiply the remainder by the specific gravity of the dip.

## EXPERIMENTAL WORK WITH METHODS OF ANALYSIS.

Much experimental work was done in developing and testing the previously described methods of analysis. A brief outline of some of this experimental work, with a more detailed discussion of certain results, may be of interest.

### DETERMINATION OF PHENOLS.

Particular difficulty was experienced with phenols. It early became clear that the most desirable method of finally estimating their amount would be by measuring the increase of volume shown by a solution of caustic soda when the phenols in question were absorbed by it. The general reasons for this conclusion have already been discussed. Attention will now be paid to some special points involved.

I. When weighed amounts of pure phenols are shaken in the measuring tube as described, and the coefficient $\frac{\text{weight phenols}}{\text{volume increase NaOH}}$ determined, it was found that—

(*a*) This coefficient is constant for a given phenol irrespective of the amount measured—within the limits of the tube—and of the presence or absence of other coal-tar hydrocarbons in addition to benzol. To illustrate, weighed amounts of a fairly pure cresylic acid were dissolved in benzol and shaken in the measuring tube with caustic soda, with the following results:

| Weight of cresol. | Increase in volume of NaOH. | Coefficient: $\left(\frac{\text{weight phenols}}{\text{volume increase NaOH.}}\right)$ |
|---|---|---|
| *Grams.* | *Cubic centimeters.* | |
| 9.1385 | 8.66 | 1.055 |
| 9.2825 | 8.62 | 1.078 |
| 9.5160 | 8.82 | 1.079 |
| 2.3893 | 2.22 | 1.076 |
| 2.3223 | 2.19 | 1.060 |

Although approximately four times as much cresol was employed in the first three trials as in the last two, the derived coefficient is practically identical.

(*b*) This coefficient is not the same for all phenols, but varies in the same direction as the specific gravity of different phenols, though in greater ratio, accordingly varying inversely as the molecular weights of the different phenols and in approximately equal inverse ratio. For the mixtures of phenols ordinarily occurring in commercial cresylic acid and in the grades of coal-tar creosote oils commonly used for making dips, the average coefficient proved to be unity as nearly as could be determined.

II. When weighed amounts of pure phenols were shaken in a separatory funnel with water, soda, sulphuric acid, and benzol in the proportions described in the analytical method, and the phenols then brought to measurement, the coefficients in all cases were found to run parallel to those obtained in Experiment I, but to be very slightly lower; that is, water is carried by the phenols into benzol solution in amount rather more than enough to balance the amount of phenols retained by the acid aqueous layer in the separatory funnel. No loss is therefore here involved.

III. The validity of the method of measurement having been thus established, the next problem was to concentrate without loss of phenols the large volume of distillate resulting from the distillation of the acidified dip with steam to a volume sufficiently small to be introduced into the measuring tube.

(*a*) The first attempt was concentration by evaporation of the liquid after rendering it strongly alkaline. Weighed amounts of phenols were dissolved in 800 c. c. of water and 25 c. c. of caustic soda 1:3, and evaporated to 40 to 50 c. c. on the steam bath, and the phenols were then separated and brought to measurement as described. It was found that this proceeding involved a loss averaging at least 5 per cent, the percentage increasing as the molecular weights of the phenols increased. This result could be expected, for the higher phenols, being of much less solubility in dilute caustic soda, and being more weakly acid and their salts consequently more easily hydrolyzed, would naturally suffer a greater percentage of loss than the lower, more acid phenols.

(*b*) An attempt was next made to extract phenols from the distillate with benzol, then concentrate the benzol solution by distillation to a residual quantity of about 60 c. c., which was lastly brought into the measuring tube with caustic soda. Weighed amounts of phenols were brought into a 1,500 c. c. separatory funnel with 800 c. c. of water, and shaken with benzol in the amount and manner described in the analytical method (page 15), both with and without the addition of NaCl. Without addition of NaCl each extraction with benzol removes at most but 75 per cent of the phenol

present each time; with 12½ grams NaCl per 100 c. c. about 87 per cent is withdrawn, and with 25 grams per 100 c. c., between 92 and 94 per cent is taken up by the benzol in each extraction. Three extractions as described will therefore account for 99.95 per cent of the amount of phenols originally present. This was eminently satisfactory. But when the benzol extract was submitted to distillation, variable amounts of phenols were found in the distillate, the amount being almost negligible in the case of phenols of high boiling point, but considerable with the lower phenols, and especially notable in the case of benzophenol.

(*c*) Attempt was next made to hold back phenols while benzol was being distilled as described in (*b*), by the addition of a few grams of metallic sodium, the idea being to eliminate the effect of small amounts of water and at the same time to bring the phenols into a completely nonvolatile compound. This attempt was quickly abandoned, for the reaction between sodium and phenols proved very slow and incomplete, even on long standing or boiling with reflux condenser.

(*d*) It will be noted that high-boiling phenols suffer special loss by the method of (*a*) and low-boiling phenols by method (*b*), while the method of extraction of (*b*) is perfectly adequate. Therefore an attempt was made to combine the two methods by distilling off the benzol over strong caustic soda—15 c. c. of 1:2 NaOH—the idea being that the strong caustic soda would hold nearly all the phenols in combination, and afford on account of its concentration but slight opportunity for hydrolysis and formation of water vapor, while since those very phenols most subject to hydrolysis and loss from the caustic soda are those of high boiling point and but slight volatility with vapors of benzol, practically no appreciable amount of phenols would escape from the flask. This proved to be the case. Delicate qualitative tests show the presence of phenols in the distillate, but in amount far beyond the power of the measuring tube to detect.

The following table will illustrate some of the positive points brought out in Experiments I, II, and III. Purified cresol was employed, obtained in the laboratory from crude cresylic acid.

*Results of experiments upon the method for determining phenols.*

| Method of treatment. | Weight taken. | Increase of NaOH. | Coefficient: $\frac{\text{weight phenols}}{\text{volume increase NaOH.}}$ | Mean coefficient. |
|---|---|---|---|---|
| | *Grams.* | *Cubic centimeters.* | | |
| Dissolved in benzol and shaken with NaOH in tube | 6.855 | 6.69 | 1.023 | 1.019 |
| | 8.625 | 8.50 | 1.015 | |
| In separatory funnel with benzol, NaOH, and $H_2SO_4$, then as in analysis | 7.542 | 7.52 | 1.003 | 1.003 |
| | 7.773 | 7.75 | 1.003 | |
| With 800 c. c. water, 200 g. NaCl, then treated as in analysis | 8.433 | 8.30 | 1.016 | 1.004 |
| | 9.776 | 9.81 | .997 | |
| | 9.344 | 9.40 | .998 | |

It is evident, accordingly, that the method described will bring to measurement, with no loss, all the phenols present in the distillate from the dip.

### TESTS WITH COAL-TAR CREOSOTE DIPS OF KNOWN COMPOSITION.

The next undertaking was to make up a coal-tar creosote dip of accurately known composition in order to test upon it the validity in practice of the methods of analysis developed.

*Dip No. 1.*—Rosin: A fair grade of ordinary commercial rosin was employed. Weight used, 220 grams.

Hydrocarbons: Coal-tar oils, supposed to be free from phenols, shaken four times with 10 to 25 per cent caustic soda, dried over calcium chlorid, and filtered. Weight taken, 550 grams.

Pure phenols: Obtained by the purification in the laboratory of crude cresylic acid. Weight taken, 120 grams.

Caustic soda and water: One part pure NaOH dissolved in two parts water. By titration with N/2 $H_2SO_4$ and methyl orange the solution showed 24.7 per cent $Na_2O$ and 75.30 per cent water. Amount taken, 90 grams, which accordingly contained $90 \times 0.247 = 22.23$ grams $Na_2O$ and $90 \times 0.753 = 67.77$ grams water. There was also added 20 c. c. water, making the total water used 87.77 grams.

The dip accordingly contained:

| | Grams. | Per cent. |
|---|---|---|
| Water | 87.77 | 8.78 |
| Soda ($Na_2O$) | 22.23 | 2.22 |
| Rosin | 220.00 | 22.00 |
| Phenols | 120.00 | 12.00 |
| Hydrocarbons and pyridin | 550.00 | 55.00 |
| | 1,000.00 | 100.00 |

Saponification was effected in a flask connected with a reflux condenser and immersed in a water bath.

Analysis of dip No. 1 gave:

| | A. | B. | Mean. |
|---|---|---|---|
| | *Per cent.* | *Per cent.* | *Per cent.* |
| Water | 8.8 | 8.6 | 8.7 |
| Soda | 2.15 | 2.17 | 2.16 |
| Pyridin | 1.19 | 1.30 | 1.25 |
| Phenols | 11.78 | 11.74 | 11.76 |
| Rosin acids, gravimetric | 19.90 | 19.80 | 19.85 |
| Rosin acids, volumetric | (1)20.03<br>(2)19.97 | (1)19.94<br>(2)19.81 | 19.94 |

It will be noted that, as was to be expected, the amount of rosin acids found is about 90 per cent of the rosin used in the dip. The results seemed very satisfactory, except perhaps in the case of the phenols. (But see page 35.)

*Dip No. 2.*—Made up more as a dip would be made in practice. Rosin, 200 grams.

Coal-tar oils which were used gave on analysis:

| | A. | B. | Mean. |
|---|---|---|---|
| | *Per cent.* | *Per cent.* | *Per cent.* |
| Water | 0.40 | 0.50 | 0.45 |
| Pyridin | 3.35 | 3.56 | 3.45 |
| Phenols | 20.30 | 20.40 | 20.35 |
| Hydrocarbons, by difference | 75.95 | 75.54 | 75.75 |
| | 100.00 | 100.00 | 100.00 |

Amount taken, 700 grams, which would give:

| | Grams. |
|---|---|
| Water | 700×0.0045= 3.15 |
| Pyridin | 700× .0345= 24.15 |
| Phenols | 700× .2035=142.45 |
| Hydrocarbons | 700× .7575=530.25 |

Soda and water: By titration with N/2 $H_2SO_4$ and methyl orange the solution was found to contain 25.22 per cent $Na_2O$ and 74.78 per cent $H_2O$. Ninety grams of the solution were employed, giving 22.7 grams $Na_2O$ and 67.3 grams $H_2O$. There was also added 10 c. c. of water. The materials were all put together in a 1,500 c. c. flask and the latter was stoppered and shaken frequently until saponification was complete, with application of no external heat.

The dip accordingly contained:

| | Per cent. |
|---|---|
| Water (0.32+6.73+1.0) | 8.05 |
| Soda ($Na_2O$) | 2.27 |
| Pyridin | 2.42 |
| Rosin | 20.00 |
| Phenols | 14.25 |
| Coal-tar hydrocarbons | 53.01 |
| Total | 100.00 |

Analysis gave the following results:

| | A. | B. | Mean. |
|---|---|---|---|
| | *Per cent.* | *Per cent.* | *Per cent.* |
| Water | 8.10 | 8.30 | 8.20 |
| Soda | 2.28 | 2.26 | 2.27 |
| Pyridin | 2.28 | 2.21 | 2.25 |
| Rosin acids | [a]18.66 | [b]18.80 | 18.73 |
| Phenols | 14.16 | 14.06 | 14.11 |
| Hydrocarbons, by difference | 54.52 | 54.37 | 54.44 |
| | 100.00 | 100.00 | 100.00 |

[a] Volumetric. [b] Gravimetric.

Results from this dip appear very satisfactory. It should be noted that the formulas employed in the experimental dips are in no way recommended for actual use. The immediate object was not to make a superior dip, but merely to test the methods of analysis employed.

TEST WITH CRESYLIC ACID DIP OF KNOWN COMPOSITION.

The next experiments were to test in the same way the validity of the methods when applied to cresylic acid dips. Dip No. 3 was accordingly made somewhat along the lines of the U. S. P. formula for liquor cresolis compositus.

One hundred and seventy-five grams of linseed oil was saponified in a beaker with 81 grams of a solution of pure KOH, shown by titration with N/2 $H_2SO_4$ and methyl orange to contain 35.9 per cent of $K_2O$ and 64.1 per cent $H_2O$. Accordingly $81\times0.359=29.08$ grams $K_2O$, and $81\times0.641=51.92$ grams $H_2O$ were introduced. The beaker with its contents was weighed before and again after saponification, and a loss of 3.5 grams noted, leaving in the soap finally 51.92—3.5= 48.42 grams of $H_2O$. The materials employed in the soap were then—

| | Grams. |
|---|---|
| Linseed oil | 175.00 |
| Potash ($K_2O$) | 29.08 |
| Water | 48.42 |
| Total | 252.5 |

Now, taking as the mean molecular weight of the fat acids of linseed oil the number 284.7,[a] and as the molecular weight of glycerin the number 92, the mean molecular weight of linseed oil will be $3(284.7)+92-54=892.1$. The 175 grams of linseed oil will then be equivalent to—

Glycerin, $175\times\frac{92}{892}=18.03$ grams.

Fatty acid anhydrids, $175\times\frac{854-27}{892}=162.25$ grams.

But this glycerin will take up $18.03\times\frac{54}{184}=5.28$ grams $H_2O$ in the process of saponification of the linseed oil, hence the completed soap theoretically consists of—

| | Grams. |
|---|---|
| Glycerin | 18.03 |
| Fatty acid anhydrids | 162.25 |
| $K_2O$ | 29.08 |
| Water (48.42—5.28) | 43.14 |
| Total | 252.50 |

The soap was transferred to a tared liter flask with the aid of U. S. P. cresylic acid (cresylic acid from two different manufacturers being mixed in equal parts to secure a fair sample), the contents were brought to 500 grams with cresylic acid, and the flask was stoppered and frequently shaken for several days till a uniform,

[a] Lewkowitsch, J. Chemical Technology and Analysis of Oils, Fats, and Waxes, 3d Ed., vol. 1, p. 334. 1904.

clear liquid resulted. The mean of four analyses (page 34) showed the U. S. P. cresol employed to be 98.80 per cent pure. The amount used was 500—252.5=247.5 grams, containing accordingly 247.5× 0.988=244.53 grams phenols and 247.5×0.012=2.97 grams of pyridin, hydrocarbons, etc.

Analysis of the dip ought then to show:

| | Per cent. |
|---|---|
| Water | 8.63 |
| $K_2O$ | 5.82 |
| Fatty acid anhydrids | 32.45 |
| Glycerin | 3.61 |
| Phenols | 48.90 |
| Pyridin, hydrocarbons, etc | 0.59 |
| Total | 100.00 |

Actual analysis of this dip gave the following results:

| | A. | B. | Mean. |
|---|---|---|---|
| Water | 8.1 | 8.0 | 8.05 |
| $K_2O$ | 5.71 | 5.72 | 5.71 |
| Fatty acid anhydrids | 31.50 | 31.39 | 31.45 |
| Glycerin | 3.50 | 3.49 | 3.50 |
| Phenols | 48.77 | 48.98 | 48.88 |
| Pyridin | 0.28 | 0.28 | 0.28 |

## TESTS FOR NONVOLATILE ACID BODIES IN COAL-TAR CREOSOTE AND COMMERCIAL CRESYLIC ACID.

Mention has already been made of the fact (page 24) that both coal-tar oils and commercial cresylic acid may contain bodies of an acid nature, absorbed by caustic soda solution with a consequent increase in its volume, but which are not volatile with steam at 100° C. These acid bodies very probably vary in amount in different samples of oils and cresols, and may not be present in every case. Examinations were made of the coal-tar creosote oil employed in making dip No. 2, and of the U. S. P. cresol used in dip No. 3.

The coal-tar creosote oil used in preparing dip No. 2 was found to contain by distillation of the oil with steam 20.35 per cent phenols, as the mean of the two results 20.30 per cent and 20.40 per cent. The oils were then handled in another way, namely, 100 grams were distilled from an Engel flask to 300° C. The first portion of the distillate containing water was received in a small stoppered cylinder, benzol and NaCl were added, the cylinder was shaken, and after separation had taken place the benzol was pipetted out and added to the rest of the distillate. Extraction of the aqueous portion was repeated several times in the same way. The total oily distillate was made to a definite volume with benzol, an aliquot part shaken with caustic soda in the measuring tube and the increase in volume noted. Some-

what variable results were obtained, ranging between 21.80 and 23.20 for the per cent of phenols found by this method in the creosote oil.

In the examination of the U. S. P. cresol used in dip No. 3 weighed amounts of the cresol were introduced into a 150 c. c. separatory funnel, with 15 c. c. of 1:2 NaOH and 30 to 40 c. c. water, then benzol and $H_2SO_4$ added, and, in short, the last two steps of the adopted analytical method were followed in detail until the phenols were brought to measurement.

Treated in this way 9.059 grams cresol gave 9.13 c. c. increase in volume of NaOH=100.77 per cent phenols; 8.146 grams cresol gave 8.15 c. c. increase in volume of NaOH=100.05 per cent phenols. The U. S. P. cresol will then appear by this method to contain 100.41 per cent phenols, the mean of the two results obtained.

Phenols were now determined exactly as they would be in a dip, by steam distillation of weighed amounts of the U. S. P. cresol.

| Weight cresol. | Increase in volume NaOH. | Per cent phenols. |
|---|---|---|
| *Grams.* | *Grams.* | |
| 9.457 | 9.40 | 99.40 |
| 9.590 | 9.46 | 98.64 |
| 9.468 | 9.36 | 98.86 |
| 9.105 | 8.95 | 98.30 |

The mean of these results is 98.80 per cent, while the range of difference between the results is about 1 per cent of the amount of phenols operated upon. When working with nearly pure phenols it is difficult to obtain results which check as closely as desirable, for the meniscus is subject to considerable variation in shape and degree of curvature. This variation in the form of the meniscus appears to a less extent when the phenols from a cresol dip are measured, and is practically absent in case the phenols have been obtained from a creosote dip, hence readings in these cases check more closely. In practice results may reasonably be expected to check within this limit of 1 per cent of the total amount of phenols in all cases; that is, results on a cresol dip containing 50 per cent phenols agree within 0.5 per cent, and those on a creosote dip containing about 10 per cent phenols within 0.1 per cent.

It is accordingly evident that both coal-tar creosote oils and even quite pure cresylic acid may contain bodies of an acid nature, which may possibly be phenoloids, but for the determination of which, since they are not volatile with steam, there appears at present no possible means. In the actual analysis of a dip these bodies will naturally tend to increase the percentage of rosin acids found, whether the latter are determined gravimetrically or volumetrically. It is not likely, however, that in any case the percentage of rosin acids will be thus increased to a figure greater than the per cent

of rosin actually employed in making the dip, as is indicated by the result for rosin acids obtained in the analysis of dip No. 2. As already shown, the creosote oil used in this dip contained a considerable amount of nonvolatile acid bodies. The existence of these nonvolatile acid bodies was not known at the time dip No. 1 was made and analyzed. Unfortunately, no more of the purified cresylic acid used for that dip was available for examination; but inasmuch as it was prepared from a very crude commercial product, it undoubtedly contained an appreciable amount of these nonvolatile acid bodies, whose presence may account for the somewhat low results for phenols obtained in the analysis of that dip.

## SUMMARY.

In conclusion certain points may be emphasized:

1. Methods appear now available for determining with considerable accuracy the constituents of coal-tar creosote and cresylic acid dips. These methods are not especially tedious, nor, while requiring a certain amount of practice for their successful execution, do they demand complicated apparatus, exceptional skill in manipulation, or the liberal use of expensive chemicals. The results are all obtained by fairly simple volumetric processes, and the closeness with which experience in this laboratory has shown them to check, whether obtained by the same or different operators, renders the methods herein described particularly adapted to the standardization of dips.

2. Methods exactly parallel to the methods employed in the analysis of dips may be applied to the valuation of creosote oil and cresylic acid which are to be used in making dips. If a dip is properly made from analyzed materials and the dip itself then analyzed, the actual analysis of the dip will agree very closely with its calculated composition. The validity of the methods of analysis is thus doubly confirmed.

3. Furthermore, the agreement between the analysis of a dip made from analyzed materials with its calculated composition indicates that it is actually possible for a manufacturer to place on the market a dip of practically unvarying composition.

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