group (Preservol, Spirittine, hardwood tar, wood tar from Douglas fir) three are about half as toxic as coal-tar creosote. The fourth, Spirittine (Page 655, Nos. 79 and 80), proved only one-third as toxic.

Further work on Fractions III, IV, and V of coal-tar creosote indicates that Fraction III is somewhat more toxic than first reported; the other two remain essentially the same as the first work demonstrated. As the results stand to date, Fractions II and III are equally highly toxic and with beechwood creosote are the three most toxic compounds reported upon. If the volatility of Fraction I could be controlled, this fraction perhaps would prove equally as toxic as II and III.

Since the greater part of Fractions II and III distills between 215 and 305° C. we may infer that, with the possible exception of phenolic bodies in Fraction I, the more highly toxic constituents of coal-tar creosote have their boiling points between these limits. Additional tests on the two water-gas-tar distillates previously reported upon indicate that the toxic point lies somewhat higher than there indicated. The distillate of low specific gravity (0.995) is somewhat less toxic than coal-tar creosote, No. 1074, while that of high specific gravity (1.042) falls comparatively low in the toxicity scale.¹

Zinc sulfate (both by-product and commercial) compares very favorably with zinc chloride and also with coal-tar creosote.

When drawing comparisons between zinc chloride and the Bruening and Marmetschke preservative (zinc chloride + aluminium sulfate) it should be kept in mind that zinc chloride cannot be tested satisfactorily by mixing with ordinary nutrient agar, on account of its tendency to combine with the medium. With the straight zinc chloride, different tests have yielded killing points lying between 0.3 and 0.5 per cent; the Bruening and Marmetschke preservative varied between 0.4 and 0.5 per cent.

Holzhelper, although composed of such toxic constituents as zinc chloride and creosote, must be in comparatively dilute form, since its toxicity is quite low, about 11 per cent being required to prevent the growth of *Fomes annosus*.

The three petroleum oils (Page 654, No. 108) showed but slight or no toxic qualities, in that generally 40 per cent cultures nearly equalled and sometimes even excelled the growth on the check cultures.

Acknowledgments are due Mr. Howard F. Weiss, Director of the Forest Products Laboratory, Madison, Wisconsin, for certain facilities and material supplied, and to Mr. Ernest Bateman, Chemist in Forest Products, of the same Laboratory, for all data upon the physical and chemical properties of the preservatives tested.

INVESTIGATIONS IN FOREST PATHOLOGY, BUREAU OF PLANT INDUSTRY
IN COÖPERATION WITH THE FOREST PRODUCTS LABORATORY
MADISON, WISCONSIN

¹ Some preliminary tests have recently been made at the Forest Products Laboratory, Madison, Wis., on the toxicity of ten authentic water-gas-tar distillates. The approximate killing point of most of these falls considerably below, or around, that of the most toxic water-gas-tar distillate here reported.

A STUDY OF SOME RECENT METHODS FOR THE DETERMINATION OF TOTAL SULFUR IN RUBBER¹

By J. B. TUTTLE AND A. ISAACS

Received March 15, 1915

PURPOSE OF INVESTIGATION

One of the most important problems in the chemical analysis of rubber compounds is the determination of total sulfur. Many investigators have worked on this subject, with the result that different laboratories have their own methods, and comparison of results obtained by these various methods is always difficult, and at times impossible.

This Bureau is now using in its routine analysis the method of Waters and Tuttle.² In order to learn whether or not the methods for this determination which have been recently published were an improvement, either in accuracy or time required, over the one now in use, and if not, to determine wherein these methods are faulty, this present investigation was undertaken.

GENERAL CONSIDERATION

The determination of the total sulfur in rubber is far from being a simple problem, involving as it does the simultaneous determination of sulfur in a number of different substances. Sulfur may be found in vulcanized rubber compounds in any of the following forms:

- 1—Free sulfur.
- 2—Sulfur combined with rubber (*i. e.*, vulcanized rubber).
- 3—Metallic sulfates, usually lead and barium.
- 4—Metallic sulfides, usually lead and zinc.
- 5—Sulfur compounds of fatty acids (from the so-called oil substitutes, or "factis").
- 6—Sulfur in bituminous substances ("mineral rubbers").

The first and second of these are always present, and the others may or may not be, according to the nature of the compound. Any method which has for its purpose the determination of the total sulfur must be adequate to determine any or all of these in widely varying amounts. In our experience in testing material for use in the Government departments, the total sulfur has varied from 1.5 to 25 per cent; the free sulfur from practically nothing to 10 per cent; and sulfur in metallic sulfates from nothing up to 6 per cent. The rubber content varied from 20 to 90 per cent, and the quality of the rubber varied from the best to the poorest. We have no quantitative data on the other sulfur-bearing components of rubber goods, but we are certain that they are frequently present and carry appreciable quantities of sulfur.

The almost universal use of litharge (in amounts sometimes 15 and even 20 per cent) in rubber mixings may have considerable bearing on the determination of sulfur by some methods even though the litharge does not in itself contain sulfur. Its effect on the determination of total sulfur will be referred to later in the discussion of the results obtained by the methods investigated.

¹ Published by permission of the Director of the Bureau of Standards.

² Bureau of Standards, *Reprint 174*; *THIS JOURNAL*, 3 (1911), 734.

REVIEW OF RECENT METHODS

In connection with the previous publication on this subject from this Bureau,¹ a number of the methods in use at that time were investigated and discussed. Since then several new methods have been proposed. Alexander's² method involving the oxidation of the rubber with sodium peroxide was recommended by Allen³ as a "reliable rapid method." Spence and Young⁴ worked on a variation of the electrolytic oxidation first suggested by Gasparini⁵ and afterwards developed by Hinrichsen.⁶ Kaye and Sharp⁷ proposed fusing the rubber directly with a mixture of zinc oxide and potassium nitrate. Ernst Deussen⁸ offered a new idea in an attempt to determine only the free sulfur and the sulfur combined with the rubber. After decomposition with concentrated nitric acid and evaporation, he treated the residue with sodium carbonate and water, and filtered, determining the sulfur in the filtrate colorimetrically. The Joint Rubber Insulation Committee⁹ proposed a procedure for the complete analysis of rubber insulation material according to which the total sulfur is determined by fusion with a mixture of sodium peroxide and potassium carbonate. While this method was recommended for 30 per cent Para insulation compounds only, it is desirable to know whether it has a wider application. H. P. Stevens¹⁰ suggested a method for correcting for the loss of volatile sulfur in the Henriques method, by absorbing the gases from the determination in alkali and subsequently determining the sulfur thus absorbed. Utz¹¹ gave a review of the subject in which the method of Kaye and Sharp was compared with that of Frank and Marckwald.¹² He considered the two methods of equal value.

There are two general methods for determining sulfur in organic compounds which have been used to determine the sulfur in rubber, *viz.*, the Carius and the bomb methods. These are so well known that description at this time is unnecessary. Both of them are considered adequate to determine the total sulfur when modified to suit the conditions peculiar to rubber. Such modifications, however, are time-consuming and render these methods undesirable for the routine analysis of rubber goods. It was therefore not considered necessary to give analytical data in this paper.

SAMPLES

Even when the assumed total sulfur content is given, this information is not sufficient to enable one to judge the efficiency of the method, since some methods will give low results with materials contain-

ing much free sulfur. For the proper interpretation of the results by any method, the entire composition of the samples used, at least as far as the sulfur-bearing constituents are concerned, should be known and reported.

The samples used in this investigation are described in Table I. Sample A was one of the samples used

TABLE I—COMPOSITION OF SAMPLES

The figures given are approximate percentages only

Sample	Description	Rubber content	SULFUR		Mineral fillers
			Total	Free	
A	Insulation	30 Fine Para	5.0	0.5	18 Barytes
B	Suction hose	40 High grade	6.0	0.5	18 Barytes
C	Special	48 Fine Para	4.25(a)	0.6	16 Barytes 16 Litharge
D	Insulation	28.5 Fine Para	1.75	1.0	4 Litharge
E	Rubber bands	93 High grade	5.0	2.7	2 Litharge
F	Special	42 Coarse Para	8.1(a)	4	30 Sublimed lead 5 Litharge
G	Gasket	55 Poor quality	12.0	8	2 Barytes 2 Litharge
H	White tubing	20 Poor quality	21.0	9	36 Barytes

(a) The amount of sulfur added as such in Samples C and F was 2 per cent and 5.4 per cent, respectively.

in the investigations of the Joint Rubber Insulation Committee. Samples B, E, G and H were taken from deliveries on various Government contracts.¹ Sample D was prepared especially for the investigations of the Analytical Committee of the Rubber Section of the American Chemical Society. Samples C and F were specially prepared by one of the authors (J. B. Tuttle) at the factory of the Voorhees Rubber Mfg. Co., at Jersey City, N. J., for the purpose of investigating the determination of total sulfur. Great care was taken in the weighing and mixing. The composition was chosen so as to show the effect upon the analysis of the two commonly used sulfates, barytes and sublimed lead, and the vulcanization was controlled so that one of the samples should have a rather large free sulfur content. These two samples have practically the same composition as many that are frequently met with in our routine work and may therefore be considered as representative of such materials.

METHODS COMPARED

DIRECT SOLUTION METHODS—1. Spence and Young: conc. HNO₃, fuming HNO₃ and electrolysis.

2. Deussen: conc. HNO₃ and extraction with Na₂CO₃.

DIRECT FUSION METHODS—3. Alexander: Na₂O₂.

4. Joint Rubber Insulation Committee: Na₂O₂ and K₂CO₃.

5. Kaye and Sharp: ZnO and KNO₃.

SOLUTION AND FUSION METHODS—6. Frank and Marckwald: fuming HNO₃, fusion with Na₂CO₃ and KNO₃.

7. Waters and Tuttle: conc. HNO₃ and Br, fusion with Na₂CO₃ and KNO₃.

SPECIAL METHOD—8. Acetone extraction, and separate determination of free and residual sulfur.

The methods as originally described by the various investigators were followed as closely as possible. Whenever it was considered advisable to depart from the original method, the reasons therefor are given. Unless otherwise stated, 0.300 gram was taken for each determination. The "fusion mixture" used

¹ In this connection it will be of interest to note that G was taken from a delivery offered on a contract calling for 50 per cent fine Para rubber and not over 3 per cent sulfur other than that present as barytes.

¹ Waters and Tuttle, *Loc. cit.*

² *Gummi Ztg.*, **18** (1904), 729-730.

³ Allen's "Commercial Organic Analysis," 4th Ed., Vol. IV, p. 140, 1911.

⁴ *THIS JOURNAL*, **4** (1912), 413.

⁵ *Gazz. chim. ital.*, [II] **37** (1907), 426-461.

⁶ *Chem. Ztg.*, **33** (1909), 735.

⁷ *India Rubber Journal*, **44** (1913), 1189.

⁸ *Z. angew. Chem.*, **24** (1913), 494.

⁹ *THIS JOURNAL*, **5** (1914), 78.

¹⁰ *Analyst*, **39** (1914), 74; *India Rubber Journal*, **47** (1914), 785.

¹¹ *Gummi Ztg.*, **28** (1914), 631-632.

¹² *Ibid.*, **17** (1903), 71.

was composed of equal parts of sodium carbonate and potassium nitrate. Fusions were made with the gasoline gas generator described by Waters.¹ The barium sulfate precipitates were allowed to stand over night before filtering, and were ignited and weighed in porcelain crucibles. Insoluble residues were examined for sulfur, the amounts of which, if present in appreciable quantities, are given. The reagents used were tested and found to be practically free from sulfur, so that no corrections are necessary on their account. Methods 4, 6, 7 and 8 are intended to determine the total sulfur, while 1, 2, 3, and 5 are intended for the determination of sulfur other than that present as insoluble sulfates.

1—SPENCE AND YOUNG—The rubber was treated with 5 cc. of concentrated nitric acid, and heated gently. When the first reaction was over, about 50 cc. (exact amount was not specified by the authors) of fuming nitric acid were added and the solution electrolyzed. As a source of current, an 8-volt storage battery was used. This was connected directly to the platinum electrodes. The resistance of the electrolytic cell was such that the current was usually between 2 and 3 amperes, though at times it was as low as 1 ampere. After two or three hours, the current was discontinued, the electrodes removed, 1 gram of potassium nitrate² was added and the solution evaporated to dryness. The nitric acid was completely removed with hydrochloric acid by several evaporations. A few drops of hydrochloric acid were added, the residue was treated with hot water and filtered. The sulfur in the filtrate was precipitated as usual. The insoluble matter filtered off above was fused with 5 gms. of fusion mixture, extracted with hot water, filtered, and after acidification the sulfur in the filtrate was precipitated as usual.

2—DEUSSEN—The Deussen method was not followed exactly as given by the author. The rubber was treated in a porcelain crucible with concentrated nitric acid and covered. After heating for a short time, the cover was removed and the solution evaporated to dryness. The residue was treated with sodium carbonate and water, and after heating, the solution was filtered. Up to this point the original method was followed exactly. Deussen reduces the sodium sulfate to sulfide and determines the latter colorimetrically. In order to avoid any error introduced by this procedure and to obtain a better comparison with the other methods, we added potassium nitrate to the filtrate, evaporated to dryness and fused. The sulfur in the cooled melt was determined as under the Waters and Tuttle method. The insoluble residue from the sodium carbonate filtration was fused with 5 grams of fusion mixture and the sulfur determined as usual.

3—ALEXANDER—The Alexander method, as given in Allen's "Commercial Organic Analysis," is said to be rapid and reliable. The rubber is intimately

mixed with 16 grams of sodium peroxide in an iron crucible provided with a lid through which a small hole has been bored. The combustion is started by introducing through this hole a red hot iron wire. No further heating is required. When the mass is cool it is dissolved in water, the crucible, lid and wire are removed, the solution is acidified with hydrochloric acid and boiled, then filtered if necessary and the sulfate precipitated by means of barium chloride.

4—JOINT RUBBER INSULATION COMMITTEE—The rubber was fused with 4 grams of sodium peroxide and 6 grams of potassium carbonate. The cooled melt was extracted with hot water to which some bromine water had been added. The solution was filtered, acidified with hydrochloric acid and evaporated to dryness to dehydrate silica. About 400 cc. of water were added, the solution made slightly acid with hydrochloric acid, filtered, and the sulfur in the filtrate determined as usual.

5—KAYE AND SHARP—The rubber was mixed with 4 grams of zinc oxide and 2 grams of potassium nitrate, placed in a crucible (both iron and porcelain were used), and covered with a layer of zinc oxide about 1 cm. deep. This was carefully heated, at first with a low, and afterwards with a full Bunsen flame. The crucible and contents were placed in a beaker, covered with water and heated; the solution was acidified with hydrochloric acid and filtered. The sulfur in the filtrate was determined as usual.

The insoluble residue filtered off from the hydrochloric solution was fused with 5 grams of fusion mixture and the sulfur determined as under the insoluble matter in the Spence and Young method.

6—FRANK AND MARCKWALD—The rubber was treated with about 20 to 25 cc. of fuming nitric acid in a porcelain crucible, the vessel covered with a watch glass and allowed to stand over night. The solution was evaporated to dryness, the residue fused with 5 grams of fusion mixture, extracted with hot water and filtered. The filtrate was acidified with hydrochloric acid and the sulfur precipitated as usual.

7—WATERS AND TUTTLE—The rubber was treated in a porcelain crucible with 25 cc. of concentrated nitric acid saturated with bromine, the vessel covered with a watch glass and allowed to stand one hour. It was heated on a steam bath for one hour and then the cover was removed and the solution evaporated to dryness. The residue was fused with 5 grams of fusion mixture, extracted with hot water, filtered, the filtrate acidified with hydrochloric acid and the sulfur precipitated as usual.

8—EXTRACTION WITH ACETONE—Some determinations were made by extracting 2 grams of rubber with freshly distilled acetone for eight hours. The acetone solution was evaporated to dryness, distilled water and bromine added, the solution heated until colorless, filtered, and the sulfur in the filtrate determined as usual. The insoluble residue was examined for sulfur by fusing with 5 grams of fusion mixture. The amount of sulfur thus found was scarcely ever more than a few tenths of a milligram.

The extracted rubber was dried at about 60° C.

¹ THIS JOURNAL, 5 (1913), 853.

² Spence and Young add 1 gm. of sodium carbonate, but, inasmuch as this on solution is changed to sodium nitrate, we used potassium nitrate, which serves the same purpose and obviates the spattering caused by the addition of a carbonate to the hot concentrated acid.

and the sulfur determined according to the method of Waters and Tuttle. The sum of these various determinations should be the total sulfur.

DISCUSSION OF RESULTS

Although the method of Waters and Tuttle is No. 7, it has been considered advisable to discuss it first since it is the most reliable and accurate method we have found for the determination of total sulfur. The reaction proceeds slowly without any very great evolution of heat so that there is little or no chance of losing free sulfur. Even when the free sulfur is very high the method is adequate to determine it with accuracy. A large number of determinations were

than that present in the insoluble sulfates. They may be further classified, according to the method of attack employed, as follows: direct solution, direct fusion, and solution and fusion methods.

The methods which have for their object the determination of sulfur other than that present in the insoluble sulfates (Nos. 1, 2, 3, and 5), attempt to separate the insoluble sulfates by filtration. Spence and Young, Alexander, and Kaye and Sharp filter from an acid solution. The securing of correct results by this method is based upon the obviously incorrect assumption that the lead sulfate originally present would remain insoluble while that formed

RESULTS OF TESTS FOR SULFUR

METHOD	1—Spence and Young			2—Deussen			4—Joint Rubber Insulation Committee Total	5—Kaye and Sharp			6—Frank and Marckwald Total	7—Waters and Tuttle Total	8—Extraction with acetone		
	Filtrate	Residue	Total	Filtrate	Residue	Total		Filtrate	Residue	Total			Extracted	Residue	Total
A							4.90					4.87			
B							4.94								
				4.53	1.66	6.19	6.26	3.63	2.43	6.06	6.00	6.29	0.51	5.74	6.25
				4.84	1.41	6.25	6.31				6.18	6.30	0.40	5.90	6.30
				3.84	2.74	6.58					6.26	6.33	0.44	5.85	6.29
				3.89	2.65	6.54					6.28	6.35			
												6.42			
												6.42			
												6.43			
												6.44			
C				3.19	0.88	4.07	4.09	3.38	0.66	4.04	4.19	4.17	0.61	3.59	4.20
				2.55	1.52	4.07	4.13	2.45	1.68	4.13	4.20	4.18	0.63	3.60	4.23
							4.19	3.32	0.86	4.18	4.28	4.20	0.60	3.64	4.24
							4.31					4.22			
												4.23			
							1.23					4.25			
D							1.76					1.67			
							1.78					1.70			
							1.80					1.73			
							1.81					1.75			
							1.83					1.78			
E	4.91											4.95			
												5.15			
												5.22			
F	5.39	2.33	7.71	7.47	0.47	7.94	7.78	6.89	0.21	7.10	7.72	7.90	3.59(a)	4.22	7.81
	6.90	0.88	7.78	7.74	0.22	7.96	7.80	6.81	0.38	7.19	7.78	7.96	3.26(a)	4.81	8.07
	6.42	1.36	7.78				7.83				7.80	7.96	4.02	4.06	8.08
	5.04	2.75	7.79				8.01				7.86	7.96	4.04	4.04	8.08
	4.67	3.17	7.84				8.02				7.88	8.00			
	5.05	2.81	7.86									8.01			
	4.52	3.38	7.90									8.02			
	4.71	3.26	7.97									8.09			
												8.11			
												8.12			
												8.12			
												8.13			
G	11.49	0.35	11.84	5.52	4.04	9.56	10.98	9.89	0.04	9.93	11.56	11.96	8.31	3.69	12.00
	11.45	0.40	11.85	5.51	4.71	10.22	11.34	9.77	0.57	10.34	11.64	12.00	8.14	3.88	12.02
	11.46	0.39	11.85	8.33	2.81	11.14	12.04	9.80	0.55	10.35		12.04	8.06	3.97	12.03
	11.52	0.34	11.86	7.96	3.43	11.39	12.10	10.74	0.03	10.77		12.08			
	11.36	0.53	11.89					10.42	0.41	10.83		12.16			
	11.57	0.32	11.89									12.18			
	11.43	0.47	11.90									12.19			
	11.56	0.34	11.90									12.20			
	11.47	0.45	11.92									12.23			
	11.44	0.48	11.92									12.29			
H				15.77	4.94	20.71	20.52	15.68	5.20	20.88	20.71	21.09	9.60	11.52	21.12
				15.69	5.16	20.85	20.68					21.16			
							20.74					21.20			
							20.83					21.30			
												21.32			
												21.36			
												21.40			

(a) These samples were not completely extracted.

made, and the results are concordant and agree with the calculated results in samples of known composition.

The Waters and Tuttle method has been in use at the Bureau of Standards for a number of years, and during that time has frequently been used in determining the total sulfur in samples of known composition. The results have invariably been satisfactory even when obtained by comparatively inexperienced analysts.

The methods which have been compared in the course of this investigation may be divided into two classes, *viz.*, those for the determination of the total sulfur, and those for the determination of sulfur other

from the litharge would be completely dissolved. Deussen filters from an alkaline carbonate solution, but this procedure is open to the objection that lead sulfate will react with sodium carbonate solution with the formation of soluble sodium sulfate. It is apparent, therefore, that such methods cannot give reliable results since their basic principles are faulty.

Considering the methods as classified according to the mode of attack, we find that the direct solution methods (Nos. 1 and 2) employ concentrated nitric acid. The use of this reagent in the determination of the total sulfur in rubber was first suggested by Henriques, and many investigators have shown that its use gives low results, probably on account

of the loss of free sulfur. Even when the sulfur which is remaining in the insoluble residue is included with that in the filtrate, the sum does not equal the calculated value.

The direct fusion methods (Nos. 3, 4, and 5) give results which are satisfactory only when the free sulfur content is relatively low. In view of the results obtained by the other fusion methods, it was not considered necessary to make any determinations by the Alexander method. The reaction between rubber and sodium peroxide often proceeds with explosive violence, particularly so when, as in this method, the sodium peroxide is not diluted with some less active flux. The more important points have been demonstrated by the results on the other methods, namely, (1)—that the direct fusion may give low results, and (2)—that the filtering of the solution of the melt after the addition of acid gives results which have no relation to the sulfur it is desired to determine.

Although the reaction during the fusion in the Kaye and Sharp method is not attended by an explosion, the results show that it is open to all the other objections which have been made above; hence it cannot be relied upon to give results which have any significance.

The results obtained by the method of the Joint Rubber Insulation Committee (No. 4) are accurate when the free sulfur is low, as it is in insulation compounds, so that it may be relied upon to do all that this committee has claimed for it. This has been also substantiated by the work of the Analytical Committee of the Rubber Section of the American Chemical Society.¹ Whenever the free sulfur content is high, our results indicate that this method has the same serious defect as the other direct fusion methods.

The methods which require both solution and fusion yield the most satisfactory results. One of these (the Waters and Tuttle method) has already been referred to. The Frank and Marckwald method is at times very satisfactory, but unfortunately it does not seem reliable with large amounts of free sulfur. The reaction between the rubber and the fuming nitric acid is at times very violent and considerable heat is evolved. In fact in several cases, by adding only 1 or 2 cc. of the acid, the heat was so great as to cause the rubber to take fire. It seems probable that this heating is responsible for the loss of sulfur and the consequent low results.

In view of the fact that the free sulfur can be determined by several methods (one of which has already been described) with considerable accuracy in the acetone extract, and since this determination is usually made in analyses of vulcanized rubber goods, it is possible, and in some cases may be convenient, to determine the total sulfur by adding to the result for free sulfur, the amount found in the residue after acetone extraction. Such a method would have the advantage of first removing the free sulfur, which has been found to be one of the most disturbing factors in many of the methods for the determination of total

sulfur. Our experience indicates that accurate results can be obtained by this method.

We have determined the sulfur remaining in the rubber after the acetone extraction, by the Waters and Tuttle method. It is more than possible that other methods will be equally efficient.

OUTLINE OF THE METHOD ADOPTED BY THE BUREAU OF STANDARDS

As the result of this and other investigations and the experience of the Bureau of Standards, extending over some years, we believe that the Waters and Tuttle method is the most reliable and it has been adopted for use in the routine work there. The determination is made as follows:

Half a gram of rubber is placed in a porcelain crucible of about 100 cc. capacity, 20 to 25 cc. of concentrated nitric acid which has been saturated with bromine, are added, the crucible covered and allowed to stand for 1 hour. It is then heated gently for 1 hour, after which the cover is removed, rinsing it with a little distilled water, and the solution is evaporated to dryness.

Five grams of fusion mixture (1 potassium nitrate : 1 sodium carbonate) and 3 or 4 cc. of distilled water are added, the mixture is digested for a few moments on the steam bath and then spread halfway up the side of the crucible to facilitate drying. The drying is done on a steam bath or electric hot plate; in the latter case care is taken to avoid spattering caused by possible overheating. When dry, the mixture is fused over a sulfur-free flame until all the organic matter has been destroyed and the melt is quite soft. The crucible and contents are cooled, placed in a 600 cc. beaker, covered with distilled water and heated on the steam bath for 3 or 4 hrs. The solution is then filtered and the insoluble matter washed thoroughly. The combined filtrate and washings should amount to about 500 cc. About 7 or 8 cc. of concentrated hydrochloric acid are added, the beaker covered, and the solution heated almost to boiling. The solution is now tested and if necessary made slightly acid toward Congo paper; if the directions have been followed exactly, there should be a slight excess of acid present. Ten cc. of 10 per cent barium chloride solution are added, and the solution is allowed to stand over night. The precipitated barium sulfate is filtered off and ignited over a small Bunsen flame, care being taken to see that the filter paper does not inflame. The barium sulfate is calculated to sulfur by means of the factor 0.1374.

SUMMARY

It is shown that the methods which have been proposed for the determination of the total sulfur other than that present as insoluble metallic sulfates, are not satisfactory.

It is shown that loss of sulfur is likely to occur in the direct fusion methods, and this loss is apt to increase with increasing free-sulfur content.

The method of Waters and Tuttle is recommended for the determination of total sulfur. This method is accurate and comparatively rapid, and has given

¹ THIS JOURNAL, 6 (1914), 514-518.

satisfactory results in the hands of a number of analysts over a rather extended period of time.

A new suggestion is offered, namely, to determine separately the free sulfur and the sulfur remaining after the acetone extraction, reporting the sum of the two quantities as the total sulfur. This procedure eliminates the troublesome effect of the free sulfur upon the determination of the total sulfur.

The authors wish to express their appreciation of the many suggestions made by Dr. C. E. Waters, of this Bureau, and of the assistance given by the Voorhees Rubber Mfg. Co., of Jersey City, in permitting us to make up some compounds of known composition in their factory.

BUREAU OF STANDARDS, WASHINGTON, D. C.

PRELIMINARY EXPERIMENTS ON THE EFFECT OF TEMPERATURE CONTROL ON THE YIELD OF PRODUCTS IN THE DESTRUCTIVE DISTILLATION OF HARDWOOD

By R. C. PALMER¹

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It is well known that in the destructive distillation of wood the products methyl alcohol and acetic acid are formed by a decomposition of the wood substance and that the reaction is accompanied by an evolution of heat. The heat supplied by the exothermic character of the decomposition when added to the heat furnished from some external source, tends to raise the temperature at which the reaction is taking place. Increasing the temperature of the wood beyond the point where spontaneous decomposition takes place will increase the speed or violence of the reaction, and this condition in turn will accelerate the rate at which the temperature is further increased.

There can be no doubt that subjecting the methyl alcohol and acetic acid to an excessive temperature at the moment of formation may result either in an immediate decomposition of some of these products or may prevent their formation from some intermediate products, and probably increases the tendency for many secondary reactions to take place.

Several facts would seem to fully substantiate this viewpoint. The yield of alcohol and acid in the destructive distillation of wood is much less than the proportion of methoxy and acetyl groupings would lead one to expect. Small scale distillations, where the opportunity for secondary decomposition and inter-reactions are minimized by better control, frequently yield much more acid or alcohol than the usual commercial distillations.

These fundamental considerations indicate that the speed and temperature of the destructive distillation reaction have an important effect on the formation of alcohol and acid. It would seem then that the amount of these products could be materially increased:

1—By causing the reaction to take place at as low a temperature as possible.

2—By decreasing the speed of the reaction.

These two methods may be in effect the same under certain circumstances, owing to the exothermic nature

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of the reaction, since low temperature distillation is a result of slowing down the reaction.

The fact that increasing the time of distillation will increase the yield of valuable products is generally known in commercial wood distillation practice. Lengthening the time of the complete process simply means slowing down the entire decomposition. In the study described in this paper, the application of temperature control to the critical stage of the decomposition has shown that a similar result may be obtained without increasing the time.¹

EXPERIMENTAL

In making a large number of destructive distillations² in laboratory apparatus as a part of studies on the relative value of different species of hardwoods, it became apparent that the temperature at which the reaction took place and the critical stage had as much influence on the yield of products as the theoretical considerations would indicate.

A more detailed laboratory study of this interpretation of temperature control was therefore made. The basic principles developed were then applied to a commercial plant in order to determine their practicability. The experiments were carried on at the Forest Products Laboratory,³ Madison, Wis., and in the plant of the Cleveland Cliffs Chemical Company, Gladstone, Mich., as a part of a series of studies on methods of increasing the yields of valuable products in the destructive distillation of hardwoods.

This opportunity is taken to acknowledge the assistance and many helpful suggestions of Mr. H. C. Merriam, operating superintendent in the wood distillation plant of the Cleveland Cliffs Iron Company, in conducting the commercial experiment and interpreting and applying the results.

PART I—LABORATORY DISTILLATION

APPARATUS—The retort used in the laboratory studies is shown in Fig. 1. This retort (A) held approximately 80 lbs. of wood. The oil jacket (B) completely surrounded the circumference of the retort, the ends being insulated with heavy asbestos packing. The oil was heated by means of a row of 20 Bunsen burners, the flame playing largely on the side of the oil jacket, as in this way it was found that a fairly good natural circulation of the hot oil could be obtained. By means of the Bunsen burners the temperature of the heating medium was controlled fairly easily.

The temperature within the retort was measured in three places: At (1) which is close to the inner shell of the retort, directly above the point where the flames play on the oil jacket; the temperature at this point was also approximately the highest temperature of the oil at all times; at (4) which is a point at the bottom

¹ Attention was first called to the effect of "slow and fast" distillation on the yield of products by Sennft, but since the comparison was made between distillation from the cold and distillation beginning with red hot retorts, the results could not be interpreted to actual practice.

² A detailed description of methods of distilling the wood and analysis of products is given in United States Department of Agriculture, *Bull.* 129, "Yields from the Destructive Distillation of Certain Hardwoods."

³ Maintained by the Forest Service, U. S. Department of Agriculture, in cooperation with the University of Wisconsin.