DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS
OF THE
BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 45

A STUDY OF SOME RECENT METHODS FOR THE DETERMINATION OF TOTAL SULPHUR IN RUBBER

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[ISSUED MAY 5, 1915]

WASHINGTON
GOVERNMENT PRINTING OFFICE
1915

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By J. B. Tuttle and A. Isaacs

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I. PURPOSE OF INVESTIGATION

One of the most important problems in the chemical analysis of rubber compounds is the determination of total sulphur. 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.[1] 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, the present investigation was undertaken.

[1] Bureau of Standards, Reprint 174; J. Ind. and Eng. Chem., 3, p. 734; 1911.

II. GENERAL CONSIDERATION

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

1. Free sulphur.
2. Sulphur combined with rubber (i. e., vulcanized rubber).
3. Metallic sulphates, usually lead and barium.
4. Metallic sulphides, usually lead and zinc.
5. Sulphur compounds of fatty acids (from the so-called oil substitutes, or "factis").
6. Sulphur 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 sulphur 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 sulphur has varied from 1.5 to 25 per cent; the free sulphur from practically nothing to 10 per cent; and sulphur in metallic sulphates 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 sulphur-bearing components of rubber goods, but we are certain that they are frequently present and carry appreciable quantities of sulphur.

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 sulphur by some methods, even though the litharge does not in itself contain sulphur. Its effect on the determination of total sulphur will be referred to later in the discussion of the results obtained by the methods investigated.

III. REVIEW OF RECENT METHODS

In connection with the previous publication on this subject from this Bureau,[2] a number of the methods in use at that time were investigated and discussed. Since then several new methods have

[2] Waters and Tuttle, loc. cit.

been proposed. Alexander's[3] method, involving the oxidation of the rubber with sodium peroxide, was recommended by Allen[4] as a "reliable rapid method." Spence and Young[5] worked on a variation of the electrolytic oxidation first suggested by Gasparini,[6] and afterwards developed by Hinrichsen.[7] Kaye and Sharp[8] proposed fusing the rubber directly with a mixture of zinc oxide and potassium nitrate. Ernst Deussen[9] offered a new idea in an attempt to determine only the free sulphur and the sulphur combined with the rubber. After decomposition with concentrated nitric acid and evaporating, he treated the residue with sodium carbonate and water and filtered, determining the sulphur in the filtrate colorimetrically. The Joint Rubber Insulation Committee[10] proposed a procedure for the complete analysis of rubber insulation material according to which the total sulphur 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. Stevens[11] suggested a method for correcting for the loss of volatile sulphur in the Henriques method by absorbing the gases from the determination in alkali and subsequently determining the sulphur thus absorbed. Utz[12] gave a review of the subject in which the method of Kaye and Sharp was compared with that of Frank and Marckwald.[13] He considered the two methods of equal value.

There are two general methods for determining sulphur in organic compounds which have been used to determine the sulphur 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 sulphur when modified to suit the conditions peculiar to rubber. Such modifi-

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[3] Gummi Ztg., 18, pp. 729–730; 1904.
[4] Allen's Commercial Organic Analysis, 4th ed., Vol. IV, p. 140; 1911.
[5] J. Ind. & Eng. Chem., 4, p. 413; 1912.
[6] Gazzetta Chim. Ital., 37, II, pp. 426–461; 1907.
[7] Chem. Ztg., 33, p. 735; 1909.
[8] India Rubber J., 44, p. 1189; 1913.
[9] Zs. Angew. Chem., 24, p. 494; 1913.
[10] J. Ind. & Eng. Chem., 5, p. 78; 1914.
[11] Analyst, 39, p. 74, 1914; and India Rubber J., 47, p. 785, 1914.
[12] Gummi Ztg., 28, pp. 631–632; 1914.
[13] Gummi Ztg., 17, p. 71; 1903.

cations, 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.

IV. SAMPLES

Even when the assumed total sulphur 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 containing much free sulphur. For the proper interpretation of the results by any method the entire composition of the samples used, at least as far as the sulphur-bearing constituents are concerned, should be known and reported.

The samples used in this investigation are described in the following table:

Composition of Samples

[The figures given below are approximate percentages only]

Sample	Description	Rubber content	Total S	Free S	Mineral fillers
A	Insulation	30 fine Para	5.0	0.5	18 barytes.
B	Suction hose	40 high grade	6.0	.5	18 barytes.
C	Special	48 fine Para	[a] 4.25	.6	16 barytes, 16 litharge.
D	Insulation	28.5 fine Para	1.75	1.00	4 litharge.
E	Rubber bands	93 high grade	5.0	2.7	2 litharge.
F	Special	42 coarse Para	[a] 8.1	4.0	30 sublimed lead, 5 litharge.
G	Gasket	55 poor quality	12.0	8.0	2 barytes, 2 litharge.
H	White tubing	20 poor quality	21.0	9.0	36 barytes.

[a] The amount of sulphur added as such in samples C and F was 2 per cent and 5.4 per cent, respectively.

Sample A was one of the samples used in the investigations of the Joint Rubber Insulation Committee. Samples B, E, G, and H were taken from deliveries on various Government contracts.[14] 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 Manufacturing Co., at Jersey City, N. J., for the purpose of investigating the determination of total sulphur. Great care was taken in the weighing and mixing. The composition was chosen so

[14] 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 of sulphur other than that present as barytes.

as to show the effect upon the analysis of the two commonly used sulphates, barytes and sublimed lead, and the vulcanization was controlled so that one of the samples should have a rather large free sulphur 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.

V. METHODS COMPARED

Direct solution methods:

1. Spence and Young, concentrated HNO_3, fuming HNO_3 and electrolysis.
2. Deussen, concentrated HNO_3 and extraction with Na_2CO_3.

Direct fusion methods:

3. Alexander, Na_2O_2.
4. Joint Rubber Insulation Committee, Na_2O_2 and KNO_3.
5. Kaye and Sharp, ZnO and KNO_3.

Solution and fusion methods:

6. Frank and Marckwald, fuming HNO_3, fusion with Na_2CO_3 and KNO_3.
7. Waters and Tuttle, concentrated HNO_3 and Br, fusion with Na_2CO_3 and KNO_3.

Special method:

8. Acetone extraction, and separate determination of free and residual sulphur.

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, 0.500 gram was taken for each determination. The "fusion mixture" used was composed of equal parts of sodium carbonate and potassium nitrate. Fusions were made with the gasoline gas generator described by Waters.[15] The barium sulphate precipitates were allowed to stand over night before filtering, and were ignited and weighed in porcelain crucibles. Insoluble residues were examined for sulphur, the amounts of which, if present in appreciable quantities, are given. The reagents used were tested and found

[15] J. Ind. & Eng. Chem., 5, p. 853; 1913.

to be practically free from sulphur, so that no corrections are necessary on their account. Methods 4, 6, 7, and 8 are intended to determine the total sulphur, while 1, 2, 3, and 5 are intended for the determination of sulphur other than that present as insoluble sulphates.

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 was 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 nitrate [16] 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 sulphur in the filtrate was precipitated as usual. The insoluble matter filtered off above was fused with 5 grams of fusion mixture, extracted with hot water, filtered, and after acidification the sulphur 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 sulphate to sulphide 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 sulphur in the cooled melt was determined as

[16] Spence and Young add 1 gram 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.

under the Waters and Tuttle method. The insoluble residue from the sodium carbonate filtration was fused with 5 grams of fusion mixture and the sulphur 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, filtered if necessary, and the sulphate 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 was added, the solution made slightly acid with hydrochloric acid, filtered, and the sulphur 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 afterward 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 sulphur 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 sulphur 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 overnight. 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 sulphur 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 sulphur 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 sulphur in the filtrate determined as usual. The insoluble residue was examined for sulphur by fusing with 5 grams of fusion mixture. The amount of sulphur thus found was scarcely ever more than a few tenths of a milligram.

The extracted rubber was dried at about 60° C and the sulphur determined according to the method of Waters and Tuttle. The sum of these various determinations should be the total sulphur.

VI. RESULTS OF TESTS

Method

Sample	1			2			4	5			6	7	8		
	Filtrate	Residue	Total	Filtrate	Residue	Total	Total	Filtrate	Residue	Total	Total	Total	Extracted	Residue	Total
A	.....	.....	.....	.....	.....	.....	4.90	.....	.....	.....	.....	4.87	.....	.....	.....
	.....	.....	.....	.....	.....	.....	4.94	.....	.....	.....	.....	.....	.....	.....	.....
B	.....	.....	.....	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	.40	5.90	6.30
	.....	.....	.....	3.84	2.74	6.58	.....	.....	.....	.....	6.26	6.33	.44	5.85	6.29
	.....	.....	.....	3.89	2.65	6.54	.....	.....	.....	.....	6.28	6.35	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	6.42	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	6.42	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	6.43	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	6.44	.....	.....	.....

VI. RESULTS OF TESTS—Continued

Method—Continued

Sample	1			2			4	5			6	7	8		
	Filtrate	Residue	Total	Filtrate	Residue	Total	Total	Filtrate	Residue	Total	Total	Total	Extracted	Residue	Total
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	.63	3.60	4.23
	.....	.....	.....	.....	.....	.....	4.19	3.32	.86	4.18	4.28	4.20	.60	3.64	4.24
	.....	.....	.....	.....	.....	.....	4.31	.....	.....	.....	.....	4.22	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	4.23	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	4.25	.....	.....	.....
D	.....	.....	.....	.....	.....	.....	1.73	.....	.....	.....	.....	1.65	.....	.....	.....
	.....	.....	.....	.....	.....	.....	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	.47	7.94	7.78	6.89	.21	7.10	7.72	7.90	[a]3.59	4.22	7.81
	6.90	.88	7.78	7.74	.22	7.96	7.80	6.81	.38	7.19	7.78	7.96	[a]3.26	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	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	8.13	.....	.....	.....
	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	8.13	.....	.....	.....
G	11.49	.35	11.84	5.52	4.04	9.56	10.98	9.89	.04	9.93	11.56	11.96	8.31	3.69	12.00
	11.45	.40	11.85	5.51	4.71	10.22	11.34	9.77	.57	10.34	11.64	12.00	8.14	3.88	12.02
	11.46	.39	11.85	8.33	2.81	11.14	12.04	9.80	.55	10.35	.....	12.04	8.06	3.97	12.03
	11.52	.34	11.86	7.96	3.43	11.39	12.10	10.74	.03	10.77	.....	12.08	.....	.....	.....
	11.36	.53	11.89	.....	.....	.....	.....	10.42	.41	10.83	.....	12.16	.....	.....	.....
	11.57	.32	11.89	.....	.....	.....	.....	.....	.....	.....	.....	12.18	.....	.....	.....
	11.43	.47	11.90	.....	.....	.....	.....	.....	.....	.....	.....	12.19	.....	.....	.....
	11.56	.34	11.90	.....	.....	.....	.....	.....	.....	.....	.....	12.20	.....	.....	.....
	11.47	.45	11.92	.....	.....	.....	.....	.....	.....	.....	.....	12.23	.....	.....	.....
	11.44	.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 two samples were not completely extracted.

VII. 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 sulphur. The reaction proceeds slowly without any very great evolution of heat so that there is little or no chance of losing free sulphur. Even when the free sulphur is very high the method is adequate to determine it with accuracy. A large number of determinations were 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 sulphur in samples of known composition. The results have invariably been satisfactory even when obtained by comparatively inexperienced analysts.

The methods wnich have been compared in the course of this investigation may be divided into two classes, viz, those for the determination of the total sulphur and those for the determination of sulphur other than that present in the insoluble sulphates. 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 sulphur other than that present in the insoluble sulphates (Nos. 1, 2, 3, and 5) attempt to separate the insoluble sulphates 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 sulphate originally present would remain insoluble while that formed from the litharge would be completely dissolved. Deussen filters from an alkaline carbonate solution, but this procedure is open to the objection that lead sulphate will react with sodium carbonate solution with the formation of soluble sodium sulphate. 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 sulphur 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 sulphur. Even when the sulphur 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 sulphur 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, first, that the direct fusion may give low results, and second, that the filtering of the solution of the melt after the addition of acid gives results which have no relation to the sulphur it is desired to determine.

Although the reaction during the fusion in the Kaye and Sharp method is not attended by any explosion, the results show that it is open to all the other objections which have been made above, hence it can not 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 sulphur 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.[17] Whenever the free-sulphur 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

[17] J. Ind. and Eng. Chem., 6, pp. 514–518; 1914.

method is at times very satisfactory, but unfortunately it does not seem reliable with large amounts of free sulphur. 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 sulphur and the consequent low results.

In view of the fact that the free sulphur 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 sulphur by adding to the result for free sulphur the amount found in the residue after acetone extraction. Such a method would have the advantage of first removing the free sulphur, which has been found to be one of the most disturbing factors in many of the methods for the determination of total sulphur. Our experience indicates that accurate results can be obtained by this method.

We have determined the sulphur 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.

VIII. 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 is added, the crucible covered and allowed to stand for one hour. It is then heated gently for one hour, after which the cover is removed, rinsed with a little distilled water, and the solution is evaporated to dryness.

Five grams of fusion mixture (1–1 potassium nitrate and 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 either on a steam bath or electric hot plate, in the latter case care being taken to avoid spattering, caused by possible overheating. When dry the mixture is fused over a sulphur-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 three or four hours. 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 is 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 cubic centimeters of 10 per cent barium chloride solution is added, and the solution is allowed to stand overnight. The precipitated barium sulphate is filtered off, and ignited over a small Bunsen flame, care being taken to see that the filter paper does not inflame. The barium sulphate is calculated to sulphur by means of the factor 0.1374.

IX. SUMMARY

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

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

The method of Waters and Tuttle is recommended for the determination of total sulphur. This method is accurate and comparatively rapid, and has given 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 sulphur and the sulphur remaining after the acetone extraction, reporting the sum of the two quantities as the total sulphur. This procedure eliminates the troublesome effect of the free sulphur upon the determination of the total sulphur.

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 Manufacturing Co., of Jersey City, N. J., in permitting us to make up some compounds of known composition in their factory.

WASHINGTON, December 1, 1914.