

DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS

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TECHNOLOGIC PAPERS OF THE BUREAU OF STANDARDS, No. 64

(Issued January 21, 1916)

DETERMINATION OF BARIUM CARBONATE AND BARIUM SULPHATE IN VULCANIZED RUBBER GOODS

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I. PURPOSE OF THE INVESTIGATION

With the advent of buying rubber goods on specifications it became necessary to develop methods which would accurately determine the various constituents. One of the most important determinations is that of total sulphur. In a recent publication of this Bureau¹ the sulphur-bearing constituents of vulcanized rubber goods were mentioned, and a method was given for a quantitative determination of the sulphur which they contain. In this article it was stated that sulphur may occur in various forms including metallic sulphates, usually lead and barium. Many specifications now permit the use of barium sulphate (barytes) without having the sulphur which it contains count as part of the specified total sulphur. It is therefore necessary to be able to determine the percentage of this mineral. This was not at all difficult as long as the rubber compounds contained barium only in the form of the sulphate. When, however, manufacturers

¹ Bureau of Standards Technologic Paper No. 45; J. Ind. Eng. Chem., 7, p. 658 (1915).
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began using the carbonate as well as the sulphate the problem became much more complex, since it became necessary to determine both salts of barium in the presence of each other, as well as in the presence of other sulphur-bearing minerals. It is with this phase of the problem that the present article deals.

II. GENERAL CONSIDERATION

The separation of barium carbonate from barium sulphate in the absence of other minerals is readily accomplished by solution of the carbonate in acids, such as hydrochloric, acetic, etc. In rubber compounds, however, this method is not applicable, since lead sulphate may be present, in which case part of the lead sulphate will also be dissolved, and the reaction between the lead sulphate in solution and the barium will cause the precipitation of barium sulphate, and the results obtained will be low. Lead sulphate may be dissolved in ammonium acetate, and it was thought that this disturbing constituent could be eliminated by this procedure, which, however, was found to be too slow and unreliable to be an acceptable method. However, still another procedure is available, viz, transforming the lead sulphate to the carbonate by boiling with alkaline carbonates, and filtering off the soluble sulphates. Sodium carbonate readily converts lead sulphate and barium sulphate ² into their carbonates; ammonium carbonate reacts with lead sulphate, but tests made here show that it has only a slight effect on barium sulphate. By treatment with ammonium carbonate, we can therefore change the lead sulphate into the carbonate, and then filter the soluble sulphates from the lead carbonate, barium carbonate, and barium sulphate. Calcium and zinc carbonates, which may be present, do not interfere with the desired separation.

III. SAMPLES

The four samples used in this investigation were of known composition, having been compounded and vulcanized at this Bureau. Their composition was as follows:

² Noyes and Bray, *J. Am. Chem. Soc.*, **29**, p. 151 (1907), state that 80 per cent of barium sulphate is converted into barium carbonate when boiled with an excess of sodium carbonate.

TABLE 1
Composition of Samples

	Compound No. 1	Compound No. 13	Compound No. 16	Compound No. 17
	Per cent	Per cent	Per cent	Per cent
Fine Para rubber.....	39.6	30.0	20.0
Plantation rubber.....				40.0
Sulphur.....	2.5	3.0	2.0	4.0
Litharge.....	8.6	7.0	8.0	8.0
Zinc oxide.....	8.7	20.0	20.0	15.0
Sublimed white lead.....	30.6
Barium carbonate.....	10.0	10.0
Barium sulphate.....	20.0	30.0	20.0
Whiting.....	20.0	20.0
Vaseline.....	3.0
	100.0	100.0	100.0	100.0

The barium carbonate used in No. 1 and No. 17 was Merck's best quality, and was finely ground before compounding. The barium sulphate was tested and found to contain practically no soluble barium salts. It will be noted that No. 1 contained both barium carbonate and lead sulphate; No. 17 barium carbonate and barium sulphate; while No. 13 and 16 contained barium sulphate only.

IV. THE METHOD EMPLOYED

Schaeffer³ has shown that the organic matter in rubber can be removed by ignition in an atmosphere of carbon dioxide without change of sulphur to sulphide, or of either to sulphate. Slight reduction of barium sulphate to sulphide may occur during ignition of the rubber, but experience shows that the amount of sulphide formed is practically negligible. The apparatus used for the decomposition of the rubber was practically the same as that used by Schaeffer, the only change being that the sample was placed in a porcelain boat so as to facilitate the removal of the residue from the glass tube. One gram of the rubber was taken for each determination. After ignition and cooling in carbon dioxide the boat was removed, the residue finely ground in an agate mortar, transferred to a 250 cc beaker, and treated with

³ J. Ind. Eng. Chem., 4, p. 837 (1912).

5 to 10 g ammonium carbonate, 15 to 20 cc of strong ammonia water, and about 50 cc of distilled water. The mixture was boiled for 15 to 30 minutes, filtered, and the precipitate thoroughly washed to remove all soluble sulphates. The residue on the filter paper was washed back into the original beaker with distilled water, about 10 cc of glacial acetic acid and sufficient water to make the total volume of the solution about 100 cc were added. This was heated to boiling and then filtered through the same filter paper as before. By this procedure, lead, barium, calcium, and zinc carbonates pass into solution, while barium sulphate and lead sulphide are not attacked. Hydrogen sulphide was passed into the filtrate, the lead sulphide filtered off, the filtrate heated on the steam bath, and 10 cc of 10 per cent sulphuric acid added. The solution was allowed to stand overnight on the steam bath; the next day the precipitate was filtered off, ignited in a porcelain crucible, cooled, and weighed.

V. RESULTS

TABLE 2

Results of Barium Carbonate Determination

[All results are expressed in percentages of the original sample]

Sample	Constituents	Present	Found			
1.....	Barium carbonate.....	10.0	9.72	9.67	9.98	10.02
	Sulphur equivalent to BaCO ₃	1.63	1.58	1.57	1.62	1.63
17.....	Barium carbonate.....	10.0	10.28	9.76	10.73	10.71
	Sulphur equivalent to BaCO ₃	1.63	1.67	1.59	1.74	1.74
13.....	Barium carbonate.....	0.0	0.17	0.08	0.17	0.25
	Sulphur equivalent to BaCO ₃	0.0	0.03	0.01	0.03	0.03
16.....	Barium carbonate.....	0.0	0.29	0.19	0.31	0.09
	Sulphur equivalent to BaCO ₃	0.0	0.05	0.03	0.05	0.02

VI. DISCUSSION OF RESULTS

The barium sulphate was calculated to barium carbonate, using the factor 0.845. The sulphur in the barium sulphate was also calculated, since it is desirable to know just what error will be introduced if the barium present in the form of the carbonate should be considered as being present as the sulphate. The results on sample No. 1 show that in the presence of lead sulphate (in the

sublimed white lead), barium carbonate can be determined with accuracy, the results, expressed in terms of sulphur, being within 0.05 per cent of the calculated amount. In sample No. 17 we have present both the sulphate and carbonate of barium, and while the results are not as good as those obtained on sample No. 1, they are sufficiently accurate for all practical purposes, the maximum error on sulphur being only 0.11 per cent. Results slightly higher than those calculated must be expected, since samples Nos. 13 and 16, which contain barium sulphate and no barium carbonate, yield small amounts of precipitate by this method, partly in consequence of slight reduction of barium sulphate to sulphide during the ignition of the rubber, and partly on account of the slight action of ammonium carbonate on barium sulphate. These amounts, in themselves, are negligible. It is apparent, therefore, that neither lead sulphate nor barium sulphate interferes appreciably with the determination of barium carbonate by this procedure.

METHOD FINALLY ADOPTED.—The total barium in the rubber compound is determined as barium sulphate by the method for the determination of barytes in use at this Bureau.⁴ This method was first suggested by C. E. Waters, and afterwards modified by W. H. Smith and the author. Barium carbonate is determined in a separate sample by the method just described, and an equivalent amount of barium sulphate is deducted from the total barium sulphate. The sulphur in the remaining portion of barium sulphate is calculated, and the total sulphur determination is corrected by this amount.

VII. SUMMARY

A new method is given for the determination of barium carbonate in vulcanized rubber goods. It is shown that this method is sufficiently accurate in the presence of lead and barium sulphates.

The author wishes to acknowledge the assistance of H. A. Ehrman, of this Bureau, who very kindly compounded and vulcanized the samples used in this investigation.

WASHINGTON, November 3, 1915.

⁴ Bureau of Standards Circular No. 38, 3d ed., p. 68 (1915); *India Rubber World*, 51, p. 128 (1914).

