

EVOLUTION OF HYDROGEN SULPHIDE FROM VULCANIZED RUBBER

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ABSTRACT

The rubber-sulphur compound in vulcanized rubber splits off hydrogen sulphide at all times and at all temperatures between 25° C. and the temperature of complete thermal decomposition. The rate of evolution of the gas depends upon the temperature, time, the proportion of combined sulphur, and possibly other factors. The reaction affords a new explanation of the formation of hydrogen sulphide during vulcanization, and possibly also, in part at least, of the excess of combined sulphur over that required by the formula C_5H_8S . It may also be another factor in aging, though, perhaps, only a minor one, and presents a new problem in the regeneration of rubber.

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I. INTRODUCTION

In the course of some experiments on the devulcanization of rubber, evidence of the liberation of hydrogen sulphide from the heated rubber was obtained. Questions immediately arose as to the extent and the conditions under which hydrogen sulphide is liberated from vulcanized rubber at elevated temperatures, and the bearing of this reaction on the desulphurization and regeneration of rubber.

The scientific literature affords very little information on this subject. Furthermore, the testimony of different writers is very conflicting and, on the whole, unsatisfactory.

II. SURVEY OF PAST WORK

Payen¹ long ago claimed that from the beginning of the reaction of sulphur with rubber, at 135° to 160° C., and during the entire time of its continuation a slow disengagement of hydrogen sulphide takes place. He concluded that the sulphur replaces some of the hydrogen

¹ Compt. rend., 34, p. 453; 1852.

in the rubber hydrocarbon. Burghardt,² Pahl,³ and Bell⁴ (who claimed that the escape of hydrogen sulphide during vulcanization was a matter of common knowledge among rubber manufacturers) likewise adopted the "substitution" theory of vulcanization, as did also Terry⁵ at first, though later⁶ he accepted the "addition" theory of Weber and others. Bysow⁷ claimed that at temperatures up to 150° C., and, therefore, in ordinary vulcanization, there is no chemical combination between rubber and sulphur, but when the mixture is heated to 160° C. the temperature rises quickly to 215° C., with evolution of hydrogen sulphide. In the latter case, however, according to Bysow, the product is no longer vulcanized rubber, but a hard, porous, and worthless mass. Weber,⁸ on the other hand, claimed that when the purest rubber hydrocarbon is used it reacts with sulphur during vulcanization without disengaging even a trace of hydrogen sulphide, that the very small amounts of this gas which are evolved when ordinary commercial rubber is used are formed by the interaction of the "insoluble" component of rubber (C₃₀H₆₈O₁₀) with the sulphur, and that the reaction between rubber hydrocarbon and sulphur is an addition process. This view was also accepted by Schidrowitz,⁹ Perkin,¹⁰ Iterson,¹¹ Stevens,¹² and Bedford and Gray,¹³ as well as others.¹⁴ In this connection should be noted a rather surprising statement by Potts,¹⁵ who says, "Rubber has a molecule with two double bonds and the sulphur adds on with evolution of H₂S. Vulcanization is thus saturation." Is this a misstatement of Potts's views, or did he really know that hydrogen sulphide is split off from the rubber-sulphur compound? He gives no data to support the latter view.

In a recent paper Stevens and Stevens¹⁶ claim to have found combined sulphur in hard rubber considerably in excess of that required for the formula C₅H₈S; they account for the excess by assuming replacement of hydrogen to a certain extent, with the formation of some hydrogen sulphide.

In all of the above-mentioned work the various investigators were interested in the formation of hydrogen sulphide only as a part of, or incidental to, the vulcanization process, and none of them appeared to consider the possibility of the splitting off of hydrogen sulphide from the rubber-sulphur compound after the latter is formed.

Burghardt¹⁷ observed that when vulcanized rubber is decomposed by the action of oils, the free sulphur is eliminated "probably as sulphuretted hydrogen," but he submitted no data to support this surmise.

² Thorpe's Dictionary of Applied Chemistry, 2, p. 312; 1889.

³ Gummi Ztg., 15, p. 145; 1900.

⁴ Gummi Ztg., 8, No. 19, p. 3; 1894.

⁵ J. Soc. Chem. Ind., 11, p. 972; 1892.

⁶ India Rubber and Its Manufacture, p. 84; 1907.

⁷ Le Caoutchouc et la Gutta-Percha, 8, p. 5291; 1911. Gummi Ztg., 26, p. 49, 1911.

⁸ Z. angew. Chem., 7, pp. 112, 142; 1894. J. Soc. Chem. Ind., 13, p. 12; 1894. Gummi Ztg., 15, p. 280; 1901. Gummi Ztg., 16, p. 563; 1902. The Chemistry of India Rubber, pp. 86-89; 1902.

⁹ Thorpe's Dictionary of Applied Chemistry, 4, p. 585; 1913.

¹⁰ Chem. Eng. (Philadelphia), 18, p. 60; 1913.

¹¹ India Rubber J., 56, p. 455; 1918.

¹² Fourth Report on Colloid Chemistry and Its General and Industrial Applications, British Assn. Adv. Sci., p. 365; 1922.

¹³ J. Ind. Eng. Chem., 15, p. 720; 1923.

¹⁴ Editorial Note, Gummi Ztg., 8, No. 19, p. 2; 1894.

¹⁵ J. Soc. Chem. Ind., 32, p. 564; 1913.

¹⁶ J. Soc. Chem. Ind., 48, p. 55T; 1929.

¹⁷ J. Soc. Chem. Ind., 2, p. 121; 1883.

Ahrens¹⁸ assumed the splitting off of hydrogen sulphide to account for a rather large decrease in both free and combined sulphur on aging, but he likewise gave no experimental evidence to support his assumption.

Dubosc¹⁹ observed a copious evolution of hydrogen sulphide when vulcanized rubber (from automobile tires) is subjected to destructive distillation. But he did not determine the amount of hydrogen sulphide formed; he merely assumed that all of the sulphur in the rubber is eliminated in this form. It is rather unusual for such decompositions to take place completely and quantitatively. Furthermore, it is quite obvious that owing to the particular design of his apparatus, the temperatures registered by his thermometer were entirely too low; for he states that the highest temperature reached in his experiment was 245° C., at which point there was no further evolution of any gas and the rubber was completely carbonized, and, in fact, largely converted into coke, an hour and five minutes after heating was started. In the experience of the present writer, soft vulcanized rubber does not even begin to melt as 245° C., much less to char; and after being heated at 285° to 289° C. on a glycerine bath for 5 hours, although it is melted at this temperature it is still far from being completely carbonized; on the contrary, after cooling it still retains much of its rubbery character.

The above brief survey represents the state of our knowledge of the evolution of hydrogen sulphide from vulcanized rubber previous to the present work. The only one of the above-mentioned investigators who observed this reaction experimentally and apart from the vulcanization process was Dubosc, and he did little more than to identify the hydrogen sulphide qualitatively. It was believed that the reaction deserved closer study, and, accordingly, the present investigation was undertaken.

Since the completion of the work described in the following pages there has appeared a paper by Fry and Porritt²⁰ on the causes of the deterioration of hard rubber. This will be considered later in the present paper.

III. GENERAL PROCEDURE

The general procedure was to heat the rubber sample in an appropriate vessel, such as a large test tube, a small Kjeldahl flask, or a special glass cylinder, through which was passed a stream of oxygen-free nitrogen, and pass the effluent gases through a solution of lead acetate acidified with acetic acid, or in some cases, when a qualitative test only was desired, into a tube containing a strip of filter paper moistened with lead-acetate solution. The lead sulphide which was formed in the lead-acetate solution was then rinsed out into a beaker, filtered off on a weighed Gooch crucible, washed, dried at 120° C., and weighed. In a number of cases the lead sulphide thus obtained was dissolved in strong nitric acid, the solution evaporated to dryness, heated with an excess of a solution of sodium carbonate, filtered, acidified slightly with hydrochloric acid, precipitated with barium chloride, and the barium sulphate thus obtained was weighed in the usual manner. Since the two sulphur determinations thus made

¹⁸ Gummi Ztg., 28, p. 490; 1913.

¹⁹ Le Caoutchouc et la Gutta-Percha, 15, p. 9617; 1918.

²⁰ India Rubber J., 78, p. 307; 1929.

always agreed very closely, the oxidation of the lead sulphide by nitric acid and its precipitation as barium sulphate was later omitted.

The source of nitrogen was a cylinder of the commercial gas. This was washed before passing it into the vessel containing the rubber sample by leading it through two absorption tubes each containing approximately 50 ml of a nearly saturated solution of alkaline pyrogallol—10 g of pyrogallol acid dissolved in 25 ml H₂O and treated with 25 ml of a 33 per cent solution of sodium hydroxide—then through a tube containing concentrated sulphuric acid if dry nitrogen was desired, or through one or two tubes containing water if moist nitrogen was desired. Practically all of the oxygen in the nitrogen was absorbed in the first pyrogallate tube, the solution in the second tube remaining transparent and light brown in color for weeks at a time. As soon as the solution in this second tube became very dark and nearly opaque, fresh solutions were substituted in both tubes.

The absorption tubes were made of long pieces of glass tubing, about 10 mm inside diameter, held in a nearly horizontal position with the ends turned up vertically for a length of about 12 to 15 cm at each end. The nearly horizontal section of the tube was 90 to 95 cm long, and at the entering end dipped sharply downward about 2 to 3 cm below the main portion of the tube before turning upward. These tubes were usually placed at such an angle as to require about 30 seconds for the bubbles to traverse the entire length of the tube. Similar tubes were used for the absorption of the hydrogen sulphide, one such tube being generally sufficient to absorb this gas completely. When the hydrogen sulphide was evolved rapidly a second lead-acetate tube was added merely as a check on the efficiency of the first tube, but only in one case was any precipitate formed in the second tube.

The various parts of the apparatus were joined together by means of rubber connectors, but the glass parts were pushed together as close as possible so as to leave a minimum of the rubber surface exposed to the gases within the apparatus. It is not believed that any appreciable errors in the results were introduced by this arrangement. When the decomposition chamber was empty, a stream of nitrogen could be passed through the apparatus for three days and nights without forming any appreciable amount of precipitate in the lead-acetate solution.

The vessel containing the rubber sample was heated in a Freas oven for temperatures of 150° C. or less, in a glycerine bath for temperatures above 150° C. up to 290° C., and over a small free flame in the experiments on destructive distillation. The nitrogen was passed through the apparatus at the rate of about 20 to 25 bubbles per minute, and the flow of gas was continued overnight, after heating had been discontinued, to sweep out of the apparatus all of the hydrogen sulphide which had been disengaged during the heating.

IV. EXPERIMENTS

EXPERIMENT 1

A sample of soft vulcanized rubber, weighing 3.3953 g and containing 3.71 per cent of combined sulphur, 1.15 per cent of free sulphur, and no fillers or pigments, was used. This was heated for

5 hours in a stream of undried oxygen-free nitrogen in a glycerine bath at a temperature of 285° to 289° C., the effluent gases being passed into a solution of lead acetate acidified with acetic acid. The temperature of the glycerine bath was raised to 285° C. in about one hour. The presence of hydrogen sulphide in the effluent gases was first noted at a bath temperature of 124° C., and was indicated by a light-brown ring at the surface of the lead-acetate solution. The rubber melted at 270° to 275° C. The lead sulphide formed in the lead-acetate solution was filtered off on a Gooch crucible, washed, and dried. It weighed 0.1032 g, representing 0.0138 g of sulphur, or 8.38 per cent of the total sulphur in the original sample of rubber.

The lead sulphide, after being weighed, was converted into barium sulphate in the manner already described. The barium sulphate thus obtained weighed 0.1012 g. The calculated yield of barium sulphate from the lead sulphide used, is 0.1007 g.

EXPERIMENT 2

This experiment was very similar to the preceding, the chief difference being that the rubber was first extracted with acetone for 10 hours. By heating 4.9941 g of the extracted rubber at 250° C. for one and one-half hours, 0.0348 g of lead sulphide was obtained. This gives a rate of 4.6 mg of lead sulphide per gram of rubber per hour. Another sample which had not been extracted, and which was heated at the same temperature for two hours, yielded 0.0770 g of lead sulphide from 4.0834 g of rubber, or at the rate of 9.4 mg of lead sulphide per gram of rubber per hour.

Since the hydrogen sulphide is formed even in the absence of free sulphur it must come at least in part from the rubber-sulphur compound itself. The difference in the rates of evolution of the gas from extracted and unextracted rubber may be due in part to the interaction of free sulphur with some of the nonrubber components, as has been shown by the work of Bedford and Gray. It may arise also in part, as will be shown later, from the higher proportion of combined sulphur resulting from further vulcanization which undoubtedly took place.

At this point, however, the reader should be warned that a strict, quantitative comparison of the results herein described is not possible in most cases, since the experiments were not designed with that in view.

EXPERIMENT 3

For this experiment the vulcanized rubber was extracted with a number of reagents for the purpose of removing the nonrubber constituents as far as possible. It was first extracted with acetone for 12 hours, then with chloroform for six hours, after which it was digested on the steam bath for four hours with a solution of 8 g of potassium hydroxide in 175 ml of alcohol, followed by digestion for four hours with 200 ml of a 10 per cent solution of acetic acid in alcohol, and for four hours more with 200 ml of a 10 per cent aqueous solution of this acid. It was finally allowed to stand for about 16 hours in alcohol, after which it was dried in a vacuum at ordinary temperature and then once more extracted with acetone for four hours. The product after drying contained 3.35 per cent of combined

sulphur. A sample of the extracted material, weighing 6.3596 g, was heated in a stream of undried nitrogen as in the preceding experiments. The temperature was raised to 285° C. in about two hours, and then held at 285° to 290° C. for three and one-fourth hours. The lead sulphide obtained weighed 0.0792 g, representing 0.0106 g of sulphur, or 4.97 per cent of the sulphur present before heating was started. The lead sulphide here obtained was again converted into barium sulphate, and the latter weighed 0.0763 g instead of the theoretical 0.0772 g.

On repeating the experiment with another sample of rubber similarly prepared, but heating it in dry nitrogen, similar results were obtained.

EXPERIMENT 4

In this experiment an attempt was made to remove the nonrubber constituents from the crude rubber before vulcanizing. One hundred and twenty-five grams of pale crêpe were digested in an autoclave for seven hours at 200° C. with 800 ml of a 2 per cent solution of sodium hydroxide. This treatment was repeated with a fresh solution of the same composition. Then the rubber was similarly digested with two successive portions of 800 ml of a 2 per cent solution of sulphuric acid for two periods of seven hours each, followed by another digestion for seven hours with sodium hydroxide in the same manner as before. It was then digested for seven hours on the steam bath with a dilute solution of hydrochloric acid consisting of 2 volumes of water and 1 volume of concentrated HCl, then overnight with a dilute solution of ammonium hydroxide, then for 24 hours with alcohol, and finally dried in a vacuum oven at 100° C. The rubber was then mixed with 8 per cent of sulphur and vulcanized for four hours in a vulcanizing press at 40-pound steam pressure. The vulcanized rubber was crumbled on the compounding mill and digested for seven hours at room temperature in concentrated hydrochloric acid and overnight on the steam bath with dilute hydrochloric acid to remove iron introduced during milling. It was next digested on the steam bath for seven hours with water, then for 24 hours at room temperature with alcohol, dried in a vacuum oven at 100° C., and finally extracted with acetone for two days. It now contained 2.53 per cent of combined sulphur and 0.03 per cent of nitrogen, the latter being determined by Kjeldahl digestion and titration.

A sample of this rubber, weighing 18.5 g, was heated at various temperatures and for various periods of time as shown in Table 1, with the results indicated.

TABLE 1.—*Thermal decomposition of vulcanized rubber*¹

IN DRY NITROGEN

Temperatures (°C.)	Time of heating	Amounts of PbS obtained
50.....	Hours 14	Slight ring at surface of lead-acetate solution.
60.....	7	Slightly more.
80.....	7	Still more.

¹ Weight of sample, 18.5 g. Combined S, 2.53 per cent.

TABLE 1.—*Thermal decomposition of vulcanized rubber*—Continued

IN MOIST NITROGEN

Temperature (°C.)	Time of heating	Amonnts of Pbs obtained
	<i>Hours</i>	
50.....	7	None.
90.....	7	Slight ring.
90.....	7	Stronger reaction.
70.....	7	Good test.
50.....	7	None.
50.....	7	Slight reaction with lead-acetate paper.

IN DRY NITROGEN AGAIN

120.....	12	0.0062 g PbS.
140.....	15	0.0105 g PbS.

The test for hydrogen sulphide appeared to be more difficult to obtain when moist nitrogen was used instead of the dry gas. For this the writer is unable to give a satisfactory explanation. However, similar results were obtained in other experiments under similar conditions. At any rate the evidence fails to show an increased evolution of hydrogen sulphide in the presence of moisture.

EXPERIMENT 5

An attempt was made in this experiment to purify the rubber as much as possible in the latex form by means of the alkali-digestion method, essentially as recommended by Pummerer.²¹ Six hundred milliliters of ammonia-preserved latex were mixed with 600 ml of an 8 per cent solution of sodium hydroxide and 1 liter of water. The mixture was digested at about 50° C. for 48 hours, with frequent shaking during the day, in a stoppered flask from which the air had been displaced by nitrogen. At the end of the second day the flask was nearly filled with water and the rubber allowed to "cream" overnight. The lower layer (clear) was then siphoned off. This treatment was repeated three more times, but the digestion was continued for only 24 hours each time. The last time this was done the rubber failed to "cream" after several days, and 75 g of sodium chloride were dissolved in the liquid, after which the rubber separated from the aqueous solution sharply within 24 hours. After siphoning off this last solution, the rubber was washed by filling the flask with water, shaking thoroughly, allowing it to cream and siphoning off the clear solution. This cycle of operations was carried out about ten times, until the spontaneous coagulation of the rubber made further washing in this manner impracticable. As the washing proceeded it was found necessary to add increasing amounts of sodium chloride to induce separation of the rubber from the aqueous solution. At the end the aqueous solution, after being acidified with acetic acid and filtered to remove remaining particles of suspended rubber, still reduced an alkaline solution of permanganate, but did not give a distinct biuret reaction.

The rubber thus obtained was washed for a few minutes on the mill (corrugated rolls) and dried in a vacuum oven at 100° C. It

²¹ Kautschuk, 2, p. 85, 1926.

was then mixed with 8 per cent of sulphur and vulcanized in a press at 40-pound steam pressure for 6.5 hours. About 35 g of the product were crumbled on the mill and extracted for two days with acetone. The rubber then contained 7.37 per cent of sulphur (combined) and 0.03 per cent of nitrogen, the latter being determined by Kjeldahl digestion followed by a colorimetric estimation with Nessler's reagent.

A sample of this extracted product, weighing 27.6 g, was heated in a stream of dry nitrogen as shown in Table 2 with the results indicated.

TABLE 2.—*Thermal decomposition of vulcanized rubber*¹

Temperature (°C.)	Time of heating	Amount of PbS obtained	Temperature (°C.)	Time of heating	Amount of PbS obtained
	<i>Hours</i>	<i>g</i>		<i>Hours</i>	<i>g</i>
25-30.....	7	None.	140.....	18	0.0162
50.....	7	(²)	200.....	12	.1019
100.....	18	0.0013	200.....	18	.0369

¹ Weight of sample, 27.6 g. Combined S, 7.37 per cent.

² Slight ring over lead acetate.

These results show that the rate of evolution of the hydrogen sulphide increases with rise in temperature, and the last two results show that for a given temperature the rate of evolution decreases with duration of heating. Here again it should be noted, however, that the results do not show the true rates of evolution of the gas for the several temperatures, since the same sample of rubber was used throughout the experiment, and was, therefore, already partly decomposed before being subjected to each of the individual tests.

EXPERIMENT 6

Crude rubber was purified in the latex form and vulcanized as in the preceding experiment. About 40 g of the vulcanizate were crumbled on the mill and digested for 6 days at 50° to 60° C., with frequent shaking, with a solution of 15 g of potassium hydroxide in 600 ml of alcohol. The alkaline solution was then replaced with a fresh solution of the same composition, and the digestion continued for 9 days more or 15 days in all. It was then digested at 50° to 60° C. with water for 20 days, the water being changed twice daily, then for 24 hours at room temperature with two successive portions of alcohol, dried in a vacuum at room temperature, and finally extracted with acetone for 3 days. The product then contained 7.13 per cent of combined sulphur and 0.01 per cent of nitrogen.

A portion of this material weighing 28.2 g was heated in a stream of dry nitrogen, with results as shown in Table 3.

TABLE 3.—*Thermal decomposition of vulcanized rubber*¹

Temperature (°C.)	Time of heating	Amount of PbS obtained	Temperature (°C.)	Time of heating	Amount of PbS obtained
	<i>Hours</i>	<i>g</i>		<i>Hours</i>	<i>g</i>
25-30.....	48	0.0015	140.....	18	(²)
50.....	12	.0010	140.....	16	0.0087
70.....	12	.0015	200.....	6.5	.0861
100.....	16	.0032	200.....	20	(²)
120.....	12	.0109	200.....	6.5	.0195
140.....	15	.0187			

¹ Weight of sample, 28.2 g. Combined S, 7.13 per cent.

² Not determined.

These results confirm in a general way those of preceding experiments, and lead to the same general conclusions. It should be noted, however, that a distinct test for hydrogen sulphide was obtained at room temperature, a fact which had not been observed in previous experiments. This is probably due to the fact that a longer period was allowed for action and that the proportion of combined sulphur in the rubber was higher than in most of the previous experiments.

After the above heating, the sample of rubber weighed 27.2 g and contained 6.98 per cent of sulphur.

EXPERIMENT 7

Samples of the final product obtained in the last experiment were subjected to destructive distillation in an atmosphere of nitrogen. The rubber was placed in a large test tube through which a stream of oxygen-free nitrogen was passing, and heated carefully over a small free flame until the material first melted, then gradually charred, and at the end left only carbon and a heavy oil in the tube. The effluent gases were passed through an absorption tube containing lead acetate. Hydrogen sulphide was disengaged rapidly during the early part of the decomposition, so rapidly, in fact, that in some cases, when the heating was too vigorous, some of the gas escaped absorption even though two lead acetate tubes were used in series. In one such decomposition, 1.0233 g of rubber, containing 6.98 per cent of sulphur, yielded 0.2668 g of lead sulphide, representing 0.0357 g of sulphur, or 3.49 per cent of the rubber sample. The lead sulphide was converted into barium sulphate in the manner previously described. The latter compound weighed 0.2595 g, or about 99.7 per cent of the theoretical 0.2603 g. There is reason to suspect that some of the hydrogen sulphide, though very little, escaped absorption in this case, the decomposition of the rubber having been accomplished in about one and one-fourth hours.

In a second determination in which the heating covered a period of about two and one-half hours, and in which all of the hydrogen sulphide was absorbed in the first lead-acetate tube, 0.5020 g of rubber yielded 0.1423 g of lead sulphide, representing 0.0192 g of sulphur, or 3.82 per cent of the rubber sample.

It will be noted that in the last determination 54.7 per cent, or more than one-half of the sulphur in the rubber sample was split off as hydrogen sulphide, but this rubber had already lost some hydrogen sulphide, in the preceding experiment, so that the real proportion of sulphur lost in this way was actually larger than the above results indicate.

EXPERIMENT 8

Hard rubber made from pale crêpe and sulphur, and containing about 30 per cent of combined sulphur and 1 per cent of free sulphur, was used for this experiment. When freshly disintegrated, as by means of a carborundum wheel or a steel rasp, the rubber evolved hydrogen sulphide at ordinary temperatures so copiously that it could be easily detected by its odor. Lead-acetate paper suspended in a bottle containing a few grams of the hard-rubber dust was discolored immediately, and was black after 10 to 15 minutes. The rate of evolution decreased rapidly, however, and after a week or 10 days

the gas was coming off so slowly that the lead-acetate paper was discolored only after two to three hours. At the end of four months, however, the powder still evolved the gas. The above behavior was observed not only in powder prepared from freshly vulcanized hard rubber, but also in that from hard rubber which was 4 months old.

A slab of hard rubber was heated for an hour at 100° C. under a pressure of less than 1 mm and allowed to cool in this vacuum. When this rubber was converted into powder, the behavior as regards evolution of hydrogen sulphide was exactly like that already noted, so far as qualitative tests could show.

In the form of slabs, the hard rubber evolves hydrogen sulphide at room temperature much more slowly than in powdered form, but nevertheless continuously, and apparently indefinitely. Two slabs of hard rubber, about 4 months old and weighing together about 150 g, when inclosed in a jar, discolored lead-acetate paper appreciably in two hours.

A quantity of hard rubber was converted into fine shreds by means of a steel rasp, extracted with acetone for three days, or about 21 hours, and left immersed in acetone at room temperature during the three intervening nights, or 72 hours in all. It then contained 29.80 per cent of sulphur.

Twenty-five grams of the extracted material were subjected to various temperatures in a stream of dry nitrogen, with the results given in Table 4.

TABLE 4.—*Thermal decomposition of hard rubber*¹

Temperature (°C.)	Time of heating	Amount of PbS obtained	Temperature (°C.)	Time of heating	Amount of PbS obtained
	<i>Hours</i>	<i>g</i>		<i>Hours</i>	<i>g</i>
25-30-----	8	None.	100-----	7	(³)
50-----	7	(²)	100-----	14	0.0053
75-----	21	0.0018	120-----	6	.0574
100-----	18	.0165	140-----	5	.6348
140-----	3	.5723	140-----	18	(³)
140-----	5	.7258	140-----	5	.3320
25-30-----	48	(³)			

¹ Weight of sample, 25 g. Combined S, 29.8 per cent.

² Barely perceptible.

³ Not determined.

These results when compared with those of previous experiments show that the amount of hydrogen sulphide evolved increases with the proportion of combined sulphur. This is particularly noticeable at the higher temperatures.

After three months, the material which had been used in the above decomposition experiments was subjected to reduced pressure of about 28 to 30 mm at room temperature for four days, during which air was frequently admitted in order to remove the accumulated hydrogen sulphide. It was then put into a tightly stoppered bottle and a strip of lead-acetate paper was suspended within. The paper was distinctly discolored in 1 hour, light brown in 5 hours, dark brown in 24 hours, and black in 48 hours.

EXPERIMENT 9

Some of the same hard rubber which was prepared for the preceding experiment, thoroughly extracted with acetone, and containing 29.80 per cent of sulphur, was subjected to destructive distillation in a stream of nitrogen, in the same manner as already described in experiment 7 with soft rubber. From 0.2587 g of the hard rubber, 0.3556 g of lead sulphide were obtained, representing 0.0476 g of sulphur, or 61.8 per cent of the sulphur in the rubber sample.

In a second determination, 0.2599 g of the extracted hard rubber yielded 0.3607 g of lead sulphide, representing 62.4 per cent of the sulphur in the rubber sample.

EXPERIMENT 10

Two different stocks of soft rubber, one containing 3.71 per cent of combined and 1.15 per cent of free sulphur, the other containing 2.12 per cent of combined and 2.70 per cent of free sulphur, which had been vulcanized and then crumbled on the mill more than two years previously, and which had been kept in tightly closed, tinned cans, were still giving off hydrogen sulphide, as indicated by strips of lead-acetate paper suspended within the cans. The same results were obtained after these samples of rubber had been thoroughly aired by spreading them on a table for a week. To make certain that this hydrogen sulphide was not some which had been held in solution or absorbed in the rubber, 60 g portions of each of these soft rubbers were extracted with acetone for two and one-half days, in the intervals of which the rubber also stood immersed in acetone during four nights and one and one-half additional days. When placed in closed vessels these extracted rubbers still discolored strips of lead-acetate paper within three to four hours and turned them black within two to three days.

V. DISCUSSION

It is evident that all vulcanized rubber is at all times disengaging hydrogen sulphide to a greater or less extent at least at and above 25° C. This hydrogen sulphide is produced, at least in part, and in some cases unquestionably the greater part, especially at elevated temperatures, by splitting off from the rubber-sulphur compound directly—not merely during, nor as a part of the vulcanizing process, but after combination of rubber with sulphur has taken place. This is evidenced not only by the evolution of the hydrogen sulphide when there is no free sulphur present and the nonrubber constituents have been largely removed, but also by the fact that more than 60 per cent of the combined sulphur in hard rubber can be thus removed. Of course, it is possible that under the conditions of destructive distillation the decomposition may follow a different course from that at lower temperatures; but this is not at all certain. The significant fact remains that the same product, hydrogen sulphide, is formed at all temperatures from 25° C. to the temperature of complete decomposition, considerably above 300° C.

The increase in the rate of evolution of the gas with rise in temperature or proportion of combined sulphur, and its decrease with time at constant temperature, which have already been noted, are quite normal phenomena.

The influence of free sulphur and acetone-soluble nonrubber constituents has already been noted and adequately accounted for, although it is possible that these substances, as well as other impurities, may influence the results in still other ways.

Since the decomposition of the rubber-sulphur compound is going on continuously at and above ordinary temperatures, and since the rate of decomposition at constant temperature is continually decreasing it is obvious that the rate at which hydrogen sulphide will be evolved from a given sample of vulcanized rubber at any given time and temperature will depend to some extent upon the previous history of the sample and its condition or state of decomposition. For this reason the results obtained in any particular case are likely to be affected in a measure by the method of preparation or purification of the rubber sample, quite apart from the degree of purity attained. It is even possible that the degree of polymerization or depolymerization may have some influence upon this decomposition.

Since the decomposition of the rubber-sulphur compound takes place to an appreciable extent at the usual temperatures of vulcanization, it is at least partly responsible for the liberation of hydrogen sulphide during vulcanization. Furthermore, this splitting off of hydrogen sulphide from the rubber-sulphur compound during vulcanization may result in additional unsaturation in the rubber molecule, which may presumably be saturated again by taking up more sulphur. This may account for at least a part of the excess of combined sulphur above the theoretical limit required by the formula C_5H_8S , as recently noted by Stevens and Stevens.

In the absence of sulphur this unsaturation may provide further opportunity for the addition of oxygen. Both the loss of hydrogen sulphide and its replacement by oxygen, if carried far enough, would certainly result in important changes in the properties of rubber. The evolution of hydrogen sulphide at ordinary or slightly elevated temperatures is very slow, but, because of the unknown losses of hydrogen sulphide occurring between vulcanization and testing, particularly during the process of purification, and because of other factors which have not yet been evaluated, the real change may be more important than the above results indicate. When such changes continue for months and years it is conceivable that their effect upon the properties of vulcanized rubber may be quite appreciable. The spontaneous decomposition of the rubber-sulphur compound would thus appear to deserve some consideration as a possible factor in aging.

Finally, since the spontaneous decomposition of the rubber sulphur compound results in the removal from the rubber molecule of not only sulphur but also of hydrogen, this reaction presents another problem in the true regeneration of rubber from old vulcanized articles.

Fry and Porritt found that hydrogen sulphide is evolved from hard rubber at ordinary temperatures in diffused sunlight and air, due to the decomposition of the rubber-sulphur compound, and that the rate of evolution is increased by exposure to direct sunlight, as well as by a rise in temperature. These conclusions agree in the main with those reached in the present work, except as to the influence of light, which was not systematically investigated by the present writer.

That light should have some influence on this reaction is not unreasonable. Fry and Porritt, however, state that in the absence of light

they were unable to detect any evolution of hydrogen sulphide. This does not agree with the observations of the present writer, since in the majority of experiments herein described the rubber was protected from light of all kinds. Nevertheless, the evolution of hydrogen sulphide from both hard and soft rubber, in total darkness, was repeatedly observed, both at ordinary and at elevated temperatures.

VI. SUMMARY

It has been found that the rubber-sulphur compound in vulcanized rubber begins to split off hydrogen sulphide as soon as it is formed, and continues to do so at all temperatures between 25° C. and the temperature of complete decomposition of the rubber in destructive distillation above 300° C.

The rate of evolution of hydrogen sulphide from any particular sample of rubber depends upon the temperature, time, the proportion of combined sulphur, and possibly the condition of the rubber.

This reaction affords an additional explanation of the formation of hydrogen sulphide during vulcanization and, through the possible production of further unsaturation in the rubber, may afford a new explanation of at least part of the excess of combined sulphur over that required by the formula, C_5H_8S .

The reaction may also be another factor in aging, and presents a new problem in the regeneration of rubber from old, vulcanized products.

WASHINGTON, December 16, 1929.