A Study of the Relation of the Structure of 1-Mercaptobenzothiazole and its Derivatives to Their Value as Accelerators of Rubber Vulcanization

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DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE SCHOOL OF THE OHIO STATE UNIVERSITY

BY

LORIN BERYL SEBRELL

THE OHIO STATE UNIVERSITY

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INTRODUCTION

By an accelerator of rubber vulcanization is meant any compound which when added to the rubber-sulfur mixture not only shortens the time required for vulcanization but also causes a decided change in the resulting physical properties.

The first organic compound to be so used was aniline, in the year 1906. The use of this compound by Oenslager and Marks in Akron was the beginning of one of the most important periods in the history of the rubber industry. Since that time many hundreds of different organic compounds have been tried with varying degrees of success. The exact mechanism by which these accelerators bring about the desired results has not been definitely determined in all cases, although considerable progress has been made.

The present investigation consists of two parts. The first deals with the methods of preparation and the properties of a recently discovered series of accelerators. The second part is concerned with the use of these compounds in rubber, the relation of their structure to their curing power, and the mechanism by which they function as accelerators.

PART I

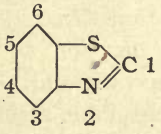
THE PREPARATION AND PROPERTIES OF 1-MERCAPTO-BENZOTHIAZOLE, ITS HOMOLOGS AND DERIVATIVES[1,2]

The present paper comprises a study of the synthesis of 1-mercapto-benzothiazole and its derivatives which was made in connection with an investigation of the role played by these compounds when functioning as accelerators of vulcanization. Eight different mercapto-benzothiazoles were prepared and studied. Each of these substances excepting where the quantity of material was limited, were prepared by four separate methods. These methods were alike in that the reaction mixture was heated in an autoclave under pressure. The reaction mixtures were as follows: (1) the corresponding disubstituted thio-urea and sulfur; (2) the zinc salt of the corresponding aryl dithiocarbamic acid and sulfur; (3) the ammonium salt of the same acid and sulfur; (4) a mixture of the corresponding aryl amine, carbon disulfide and sulfur.

The first method has been described by Romani.[3] The last three methods are new.

[1] *J. Amer. Chem. Soc.* **45**, 2390.

[2] The system of nomenclature as outlined in *C. A. Decennial Index*, **1–10**, 2345, namely, omitting the sulfur and beginning the numbering with the carbon atom of the thiazole ring has been followed throughout this article.



[3] The four methods of preparation described in the following pages as applied to 1-mercapto-benzothiazole and its three monomethyl derivatives, together with their disulfides and metallic salts were reported before the Organic Division of the American Chemical Society at the Birmingham meeting, April 6th, 1922. [(a) See *Science*, **56**, 55 (1922).] Shortly afterward, an article by Romani, [(b) *Gazz. chim. ital.*, **52**, 29 (1922)] became available, describing the preparation of the three methyl derivatives by one of the methods, namely, heating the corresponding disubstituted thio-urea with sulfur. To him, undoubtedly, belongs priority of publication of a description of these three derivatives by this one method. He did not describe the disulfides.

Historical

1-Mercapto-benzothiazole was first obtained by A. W. Hofmann[4] in an attempt to prepare the disulfhydryl derivative of thiocarbanilide by the action of carbon disulfide on *o*-aminophenol. He obtained the same substance by the action of sodium hydrosulfide on chlorophenyl mustard oil (1-chloro-benzothiazole) and also when carbon disulfide was caused to react with *o*-aminothiophenol disulfide. The product thus obtained, after recrystallization from alcohol, melted at 179° and was easily oxidized to a disulfide melting at 180°.

Jacobson and Frankenbacher[5] while studying the formation of benzothiazoles, heated azobenzene with carbon disulfide in a sealed tube at 250° for 5 hours. The product melted at 174° but was identical with Hofmann's 1-mercapto-benzothiazole. The disulfide obtained by the oxidation of this product with potassium dichromate in acetic acid solution after recrystallization from benzene melted at 186°.

In order to verify the assumption that phenyl mustard oil is an intermediate product in the formation of 1-mercapto-benzothiazole from azobenzene, these authors heated the former substance in a sealed tube with sulfur for 5 hours. The yield of mercapto-benzothiazole thus obtained was equal to 45% of the weight of mustard oil used. The constitution of the thiazole was further established by fusion with potassium hydroxide, thus regenerating *o*-aminothiophenol.

Azobenzene when heated with phenyl mustard oil was found to yield 1-anilido-benzothiazole although the same substance could not be obtained by the direct action of aniline on mercapto-benzothiazole.

Rassow, Dohle and Reim[6] have shown that 1-mercapto-benzothiazole is formed by the action of sulfur on dimethylaniline.

Bedford and Sebrell[7] as well as Bruni and Romani[8] have independently described the preparation of 1-mercapto-benzothiazole by the reaction of thiocarbanilide with sulfur when heated under pressure. More recently Romani[3b] has extended this method of preparation to the three monomethyl derivatives of 1-mercapto-benzothiazole. He recommends the use of an excess of sulfur and zinc oxide as a catalyst. Romani prepared the metallic salts of these methylated mercapto-benzothiazoles but not the disulfides.

Mechanism of the Reaction

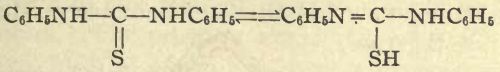
Bruni and Romani,[8] apparently following the lead of Jacobson and Frankenbacher, have sought to explain the formation of 1-mercapto-benzothiazole from thiocarbanilide, monophenyl-thio-urea and methylene-aniline upon the assumption that these substances first decompose to give phenyl mustard oil. They mention an alkali-insoluble residue, which apparently was not further investigated. It is shown in the experimental part of this paper that this insoluble residue consists chiefly of 1-anilido-benzothiazole and that it is formed in largest amounts when thiocarbanilide is used as the starting material. Indeed, it is almost entirely absent when ammonium phenyl-dithiocarbamate or the free aniline and carbon

[4] Hofmann, *Ber.*, **20**, 1788 (1887).
[5] Jacobson and Frankenbacher, *Ber.*, **24**, 1400 (1891).
[6] Rassow, Dohle and Reim, *J. prakt. Chem.*, **93**, 183 (1916).
[7] Bedford and Sebrell, *J. Ind. Eng. Chem.*, **13**, 1034 (1921).
[8] Bruni and Romani, *Giorn. chim. ind. applicata*, **3**, 351 (1921).

disulfide are used. The insoluble residue obtained when the zinc salt is used consists almost wholly of zinc sulfide.

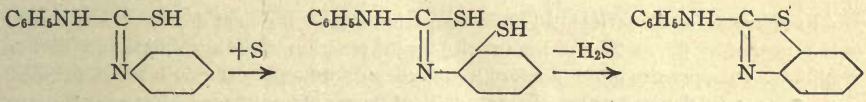
If the formation of 1-mercapto-benzothiazole from thiocarbanilide is assumed to take place through its decomposition products, such as aniline and carbon disulfide or phenyl mustard oil, by virtue of their reaction with sulfur, then little or no 1-anilido-benzothiazole should be expected since these latter reactions form only small amounts of the alkali-insoluble residue. These facts seem to indicate that direct sulfurization of the thiocarbanilide offers the most satisfactory explanation for the simultaneous formation of 1-mercapto-benzothiazole and 1-anilido-benzothiazole. The formation of these two products may be readily understood by use of the following mechanism.

1. Thiocarbanilide may be assumed to be in equilibrium with its tautomeric form.

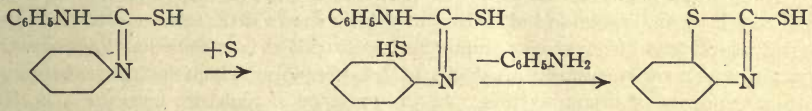


2. This tautomeric form should occur as two geometric isomers, *A* and *B*.

3. When *A* is sulfurized and hydrogen sulfide eliminated 1-anilido-benzothiazole is formed.



4. When *B* is sulfurized and aniline eliminated 1-mercapto-benzothiazole is formed.



In the experimental part of this paper it is shown that the combined yield of these two products will account for between 90 and 96% of the thiocarbanilide used. These facts are of especial significance since Jacobson and Frankenbacher have shown that 1-anilido-benzothiazole is not formed by the action of aniline on 1-mercapto-benzothiazole.

The formation of 1-mercapto-benzothiazole from phenyl-dithiocarbamic acid and its salts is not so easily traced. It may be explained in one of three ways.

1. The dithiocarbamic acid derivative may decompose with the formation of phenyl mustard oil, which in turn reacts with the sulfur to form the mercapto-benzothiazole. This explanation would correspond to that offered by Jacobson and Frankenbacher[5] and by Bruni and Romani[8] to

account for the formation of the mercapto-thiazoles in other cases. The former workers obtained a 45% yield of 1-mercapto-benzothiazole by heating phenyl mustard oil with sulfur. In this Laboratory as high as 60% yields have been obtained by the same method. By reference to Table I it will be seen that phenyl-dithiocarbamic acid and its salts yield 75 to 80% of the same thiazole. It seems doubtful, therefore, whether phenyl mustard oil is an intermediate product in the formation of mercapto-benzothiazoles from phenyl-dithiocarbamic acid and its salts.

2. Phenyl-dithiocarbamic acid and its salts not only yield phenyl mustard oil but also undergo a second type of splitting with the formation of aniline and carbon disulfide. This is especially true of the ammonium salt, since thiocarbanilide is found among its decomposition products. Thiocarbanilide should be expected to react with sulfur yielding the mercapto-thiazole according to the scheme given above. Such a reaction would produce a large amount of an alkali-insoluble residue which experiment shows is not the case.

3. There is no *a priori* reason why phenyl-dithiocarbamic acid and its salts should not undergo direct sulfurization as readily as its anilide. The present authors believe this to be a more logical explanation and that the mercapto-benzothiazole is produced by the loss of the appropriate hydrosulfide from the addition product thus formed.

Experimental Part

Preparation of Materials.—The ammonium salts of the aryl dithiocarbamic acids were prepared by the method of Losanitch,[9] by the reaction of the arylamine and carbon disulfide in the presence of ammonium hydroxide or ammonium sulfide in alcoholic solution. The rapid decomposition characteristic of these ammonium salts has caused many investigators to doubt their actual existence.

Ammonium phenyl-dithiocarbamate prepared in the presence of strong ammonium hydroxide is quite stable and after careful drying shows little tendency to decompose. By recrystallization from strong ammonium hydroxide it is obtained as long hexagonal crystals, which when carefully washed and dried have been kept for more than a year without evidence of decomposition. In the presence of moisture however it is slowly converted into thiocarbanilide, carbon disulfide and ammonia, as reported by Losanitch.

These ammonium salts may also be prepared by passing ammonia gas into a solution of aryl amine and carbon disulfide in benzene, but the method has no advantages over the one previously described.

The zinc salts of the aryl dithiocarbamic acids were prepared by adding a solution of zinc acetate in water or ammonium hydroxide to an aqueous solution of the corresponding ammonium salt. They may also be prepared by the method of Krulla[10] who added the metallic oxide to a mixture of the aniline and carbon disulfide. The first method gives the purer product.

Thiocarbanilide and its substituted derivatives were prepared by the action of the aryl amine with carbon disulfide in the usual manner. These products were purified un-

[9] Losanitch, *Ber.*, **24**, 3022 (1891); *Ann.*, **166**, 142 (1873).

[10] Krulla, *Ber.*, **46**, 2669 (1913).

til the melting points varied not more than 3° or 4° from the highest recorded values in any case.

Apparatus.—The apparatus used in this work consisted of a steel autoclave mounted in an electric resistance oven. The autoclave, which had a capacity of 2 liters, was turned from tool steel and was capable of withstanding a pressure of 2000 pounds. The oven consisted of 3 heating elements specially wound from Chromel wire and mounted on a reinforced frame built up from Alundum cement. The heating unit was effectually insulated by packing in a mixture of asbestos and magnesite. Temperature control, secured by an external hot wire rheostat, was sufficiently exact to make it possible to reproduce any given set of temperature conditions. Temperatures up to 600° were easily obtained.

Procedure.—The substance used to prepare the thiazole was mixed intimately with one molar equivalent of sulfur and placed in the autoclave. Practically all runs were made by bringing the oven to a temperature of 390–400°, then lowering the autoclave to position and allowing the temperature of the reaction mixture to rise until the pressure reached a maximum. The pressure would rise gradually with the temperature to about 170–180° where the increase became much more rapid reaching a maximum at about 225–250°. The pressure generated varied with the substance used to produce the thiazole, being greatest with the ammonium salts and least with the disubstituted thio-ureas. Reproducing the heating conditions did not always give the same yield of product. Usually the autoclave was withdrawn from the oven immediately after the pressure reached the maximum to secure more rapid cooling, and when it was quite cold the accumulation of hydrogen sulfide was blown off and the autoclave opened.

Method of Purification.—The crude reaction product was removed from the autoclave by solution in warm dil. sodium hydroxide solution. This alkaline solution was submitted to steam distillation to remove any free aryl amine. The solution was then filtered from a residue of insoluble material and fractionally precipitated by the addition of small portions of hydrochloric acid. The first precipitates were very dark and carried down most of the coloring matter. The last fractions precipitated consisted of the 1-mercapto-benzothiazole in an almost pure form. The product was redissolved in sodium carbonate solution and reprecipitated further purification varied depending upon the nature of the product and will be described for each individual substance together with its physical and chemical characteristics.

Discussion of the Experimental Results

The data collected in the preparation of 1-mercapto-benzothiazole and 6 of its substituted derivatives are set forth in Table I. Not all of the runs made are listed, but those selected are typical. Failure to prepare all the thiazoles by each of the four methods was due to a lack of sufficient quantity of the aryl amines from which to prepare the necessary starting

materials. In such cases that method was selected which promised to yield the largest amount of easily purified product.

TABLE I

DATA ON THE PREPARATION OF 1-MERCAPTO-BENZOTHIAZOLES

	Substances used	Used G.	Time Hrs.	Max. temp. °C.	Max. press. Lbs.	NaOH insol. G.	Yield G.	Yield %	Product
1	Thiocarbanilide	456	4.00	265	300	105.0	245.0	74.0	
2	Ammonium phenyl-dithiocarbamate	263	1.50	224	1000	7.3	174.5	74.0	1-Mercapto-benzothiazole
3	Zinc phenyl-dithiocarbamate	350	1.83	247	575	101.0	225.2	77.5	
4	Aniline and carbon disulfide	93							
		76	2.00	271	571	9.0	128.0	76.6	
5	Di-*o*-tolyl-thio-urea	512	4.00	293	520	194.0	177.0	49.0	
6	Ammonium *o*-tolyl-dithiocarbamate	170	1.42	253	1050	18.5	103.0	67.0	1-Mercapto-3-methyl-benzothiazole
7	Zinc *o*-tolyl-dithiocarbamate	214	1.25	266	625	137.5	65.7	37.0	
8	*o*-Toluidine and carbon disulfide	105							
		76	1.58	255	675	34.7	80.4	45.5	
9	Ammonium *m*-tolyl-dithiocarbamate	186	1.00	242	625	15.5	116.6	69.5	1-Mercapto-4-methyl-benzothiazole
10	Di-*p*-tolyl-thio urea	384	1.50	295	475	104.0	185.0	68.0	
11	Ammonium *p*-tolyl-dithiocarbamate	308	1.25	227	1050	22.8	199.2	71.5	1-Mercapto-5-methyl-benzothiazole
12	*p*-Toluidine and carbon disulfide	105							
		76	1.50	240	738	44.0	102 0	57.9	
13	2,4,2',4' - Tetramethyl-diphenyl-thio-urea	260	1.25	228	450	178.6	30.7	17.2	
14	Ammonium *o,p*-xylyl-dithiocarbamate	198	1.70	220	1000	37.1	62.1	34.5	1-Mercapto-3,5-dimethyl-benzothiazole
15	Zinc *o,p*-xylyl-dithiocarbamate	239	1.00	239	775	114.5	66.2	32.4	
16	*m*-Xylidine and carbon disulfide	121							
		76	1.58	247	725	84.0	59.3	30.4	
17	Di-*p*-phenetyl-thio urea	269	1.83	244	325	109.0	104.5	58.4	1-Mercapto-5-ethoxy-benzothiazole
18	Ammonium *p* - phenetyl - dithiocarbamate	339	1.10	206	1275	8.5	227.5	73.0	
19	Zinc *p* phenetyl-dithiocarbamate	288	1.58	246	550	125.0	147.7	59.3	
20	*p*-Phenetidine and carbon disulfide	137							
		76	1.30	249	455	49.0	117.4	55.6	
21	*p*-Anisidine and carbon disulfide	62							
		38	1.20	237	365	36.5	61.5	62.0	1-Mercapto-5-methoxy-benzothiazole

Runs 1 and 5 were made first, and without preheating the oven, thus accounting for the longer reaction time. In later runs the reaction time was shortened to avoid heat decomposition. The ammonium aryl-dithiocarbamates gave in general the best yields, but the products from the zinc salts contained less tarry material and were therefore more readily purified.

The more highly substituted the arylamine, the lower the yield of the thiazole so that only a 34.5% yield of the dimethyl derivative was obtained even from the ammonium salt of xylyl-dithiocarbamic acid.

The disubstituted thio-ureas always yielded large amounts of an alkali-insoluble by-product. The yield of this substance is markedly lower when the ammonium salt of the aryl-dithiocarbamic acid or the aryl amine

and carbon disulfide were used. In the case of the zinc salts the alkali-insoluble product consisted almost wholly of zinc sulfide.

Nature of the Alkali-Insoluble Material

In the case of thiocarbanilide the alkali-insoluble part of the reaction product was found to consist largely of 1-anilido-benzothiazole. The purification of this anilido derivative proved to be so tedious that the separation of a similar derivative was not successfully completed in any of the other cases.

1-Anilidobenzothiazole.[4]—The alkali-insoluble residue from the thiocarbanilide-sulfur reaction mixture was dissolved in alcohol and the solution poured into dil. hydrochloric acid. A small amount of acid-insoluble substance was removed by filtration and the anilido derivative precipitated by the addition of sodium hydroxide. Fifty g. of the original residue gave 36 g. of the purified anilido derivative and 5 g. of the acid-insoluble substance, which proved to be mostly 1-mercapto-benzothiazole. After recrystallization from benzene the 1-anilido-benzothiazole was obtained as light yellow crystals melting at 154°. A mixture of this product with 1-anilido-benzothiazole prepared by the action of phenyl mustard oil on azobenzene gave the same melting point.

Analyses. Subs., 0.5470: 46.9 cc. 0.1 *N* H_2SO_4. Subs., 0.5102: $BaSO_4$, 0.5293 Calc. for $C_{13}H_{10}N_2S$: N, 12.38; S, 14.16. Found: N, 12.00; S, 14.25.

Using the above data the calculated yield of pure 1-anilido-benzothiazole available from the 105 g. of alkali-insoluble residue from the thiocarbanilide in Table I is 75.6 g. or 16.5%. By combining this yield with the 73.3% of 1-mercapto-benzothiazole obtained, approximately 90.0% of the thiocarbanilide is accounted for. When one considers the losses incident to purification it is easy to conceive that the actual yield of the two derivatives is much higher, being about 96% on the basis of the crude products.

Disulfides

The disulfides of each of the mercapto-thiazoles described were prepared by the method of Hofmann.[5] An alcoholic or alkaline solution of the mercapto-thiazole was oxidized by the gradual addition of an alcoholic solution of iodine. The resulting disulfide, insoluble in alcohol or alkalies, precipitated immediately, and after it was filtered, washed and dried was purified by recrystallization from the solvent indicated in each case.

Zinc and Lead Salts

The zinc salts of the mercapto-benzothiazoles may be prepared by either of two methods. A solution of the ammonium salt may be precipitated by the addition of a solution of ammonium zincate, or an alcoholic solution of the thiazole may be precipitated by adding an aqueous solution of any zinc salt. The first method gives the purer product.

Both the normal and the basic lead salts may be prepared, depending upon the method used. The normal lead salts were obtained by precipitating an alcoholic solution of the free thiazole or an aqueous solution of its sodium salt by an aqueous solution of any soluble lead salt. The basic lead salts were obtained by precipitating an alkaline solution of the mer-

capto-benzothiazole by a solution of lead hydroxide in an excess of sodium hydroxide. These salts were thoroughly washed, dried and subjected to analysis without further purification.

The zinc and lead salts of each of the several mercapto-benzothiazoles were prepared, but in only three cases were they actually analyzed and tested for their accelerating power as indicated in the following pages.

1-Mercapto-benzothiazole[5] is soluble in alcohol, benzene and acetic acid. By recrystallization from dil. alcohol it was obtained as light yellow needles, melting at 177°.

Analyses. Subs., 0.7502: 44.8 cc. of 0.1 *N* H_2SO_4. Subs., 0.1016: $BaSO_4$, 0.2840. Calc. for $C_7H_5NS_2$: N, 8.38; S, 38.32. Found: N, 8.37; S, 38.38.

THE DISULFIDE[5]; an amorphous slightly yellow powder, melting at 176°; yield, 87%.

THE ZINC SALT; a white, amorphous powder.

Analysis. Calc. for $C_{14}H_8N_2S_4Zn$: N, 7.05; Zn, 16.45. Found: N, 7.21; Zn, 16.05.

THE NORMAL LEAD SALT; a bright yellow powder.

Analysis. Calc. for $C_{14}H_8N_2S_4Pb$: Pb, 38.40. Found: 38.49.

THE BASIC LEAD SALT; an amorphous white powder.

Analysis. Calc. for $C_7H_5NS_2OPb$: Pb, 53.05. Found: 52.35.

1-Mercapto-3-methyl-benzothiazole[3b] after repeated recrystallizations from dil. alcohol and finally from 50% acetic acid was obtained as white needles melting at 186°.

Analyses. Subs., 0.7205: 41.2 cc. of 0.1 *N* H_2SO_4. Subs., 0.1060, 0.1143: $BaSO_4$, 0.2720; 0.2929. Calc. for $C_8H_7NS_2$: N, 7.73; S, 35.36. Found: N, 8.00; S, 35.26, 35.21.

THE DISULFIDE; white needles from chloroform; m. p., 162°.

Analysis. Calc. for $C_{16}H_{12}N_2S_4$: S, 35.55. Found: 35.63, 35.48.

THE ZINC SALT; a white amorphous powder.

Analysis. Calc. for $C_{16}H_{12}N_2S_4Zn$: Zn, 15.37. Found: 15.35.

THE NORMAL LEAD SALT; an amorphous yellow powder.

Analysis. Calc. for $C_{16}H_{12}N_2S_4Pb$: Pb, 36.50. Found: 36.78.

THE BASIC LEAD SALT; an amorphous white powder.

Analysis. Calc. for $C_8H_7NS_2OPb$: Pb, 51.24. Found: 51.50.

1-Mercapto-4-methyl-benzothiazole[3b] was prepared only through the ammonium salt of *m*-tolyl-dithiocarbamic acid. After successive recrystallizations from 75% alcohol, 50% acetic acid and benzene, it was obtained as light yellow plates melting at 163°.

Analyses. Subs., 0.1585, 0.2270: $BaSO_4$, 0.4075, 0.5878. Calc. for $C_8H_7NS_2$: S, 35.36. Found: 35.30, 35.52.

THE DISULFIDE; white plates from benzene; m. p., 195°.

Analysis. Calc. for $C_{16}H_{12}N_2S_4$: S, 35.55. Found: 35.57; 35.65.

1-Mercapto-5-methyl-benzothiazole[3b] was recrystallized twice from 50% acetic acid and finally from benzene. It forms fine, very light yellow crystals melting at 181°.

Analyses. Subs., 0.7234: 38.37 cc. of 0.1 *N* H_2SO_4. Subs., 0.1860, 0.1985: $BaSO_4$, 0.4784, 0.5109. Calc. for $C_8H_7NS_2$: N, 7.73; S, 35.36. Found: N, 7.44; S, 35.39, 35.34.

THE DISULFIDE; This was insoluble in alcohol but soluble in benzene and chloroform, white needles from chloroform melting at 201–202°.

Analysis. Calc. for $C_{16}H_{12}N_2S_4$: S, 35.55. Found: 35.59.

THE ZINC SALT; a white amorphous powder.

Analysis. Calc. for $C_{16}H_{12}N_2S_4Zn$: Zn, 15.37. Found: 15.40.

1-Mercapto-3,5-dimethyl-benzothiazole was recrystallized several times from alcohol from which it separates in light yellow crystals melting at 250.5°. It is only very slightly soluble in acetic acid or benzene.

Analyses. Subs., 0.2050, 0.1888: $BaSO_4$, 0.4904, 0.4523. Calc. for $C_9H_9NS_2$: S, 32.82. Found: 32.85, 32.90.

THE DISULFIDE; fine white needles, m. p. 193°, obtained by repeated precipitation from chloroform with the gradual addition of alcohol.

Analyses. Calc. for $C_{18}H_{16}N_2S_4$: S, 32.99. Found: 33.02, 33.13.

1-Mercapto-5-ethoxy-benzothiazole was prepared by each of the four methods but only the ammonium *p*-phenetyl-dithiocarbamate yielded an easily purified product. Recrystallized from 75% alcohol and twice from benzene it was obtained as well-formed, long, cream-colored needles melting at 198°. It is only slightly soluble in benzene and other organic solvents.

Analyses. Subs., 0.1950, 0.1852: $BaSO_4$, 0.4303, 0.4044. Calc. for $C_9H_9NOS_2$: S, 30.33. Found: 30.31, 29.99.

Attempts to prepare the disulfide were unsuccessful.

1-Mercapto-5-methoxy-benzothiazole was prepared by each of the four methods but the product in all cases proved very difficult to purify. It was found that by rapidly heating the reaction mixture and rapidly cooling the autoclave a more easily purified product was obtained. Recrystallized from 70% alcohol and twice from benzene it forms light yellow needles melting at 201°.

Analysis. Subs., 0.1505: $BaSO_4$, 0.3546. Calc. for $C_8H_7NOS_2$: S, 32.48. Found: 32.37.

Attempts to prepare substituted mercapto-benzothiazoles from *o*-anisidine, the *o*- and *p*-chloro- and bromo-anilines and *p*-aminophenol were unsuccessful. Benzidine and carbon disulfide yielded an alkali-soluble product melting above 250°, which was not further investigated.

Summary and Conclusions

1. The chemistry of the zinc and ammonium salts of phenyl-dithiocarbamic acid has been extended and the work of Losanitch verified.

2. Three new methods for the preparation of 1-mercapto-benzothiazole and its substituted derivatives have been described.

3. A fourth method previously described by one of us and independently announced about the same time by Bruni of Italy, has been extended to these derivatives.

4. The mechanism of the reaction involved in the formation of 1-mercapto-benzothiazoles by the action of sulfur on disubstituted thioureas is fully discussed. Experimental evidence is offered in support of the view that this reaction takes place by virtue of direct sulfurization of the *cis*-mercapto form of thiocarbanil$_2$de and subsequent loss of the aryl amine to form the mercapto-benzothiazole. It is also pointed out that

sulfurization of the *trans*-mercapto form of thiocarbanilide and loss of hydrogen sulfide explains the simultaneous formation of anilido-benzothiazole.

5. Direct sulfurization and subsequent elimination of the corresponding hydrosulfide is offered as the best explanation of the formation of mercapto-benzothiazoles by the action of sulfur on the aryl dithiocarbamic acids and their salts.

6. Six substituted mercapto-benzothiazoles are described together with four of the corresponding disulfides.

7. Methods are given for the preparation of the zinc, normal lead and basic lead salts of the 1-mercapto-benzothiazoles and in three cases such salts are described.

PART II

1—Mercaptobenzothiazole and Its Derivatives as Accelerators of Rubber Vulcanization[1,2]

THE use of 1-mercaptobenzothiazole as an accelerator of vulcanization was first suggested by Bedford and Sebrell.[3] This announcement was closely followed by that of Bruni and Romani,[4] who set forth in detail a method for the preparation of 1-mercaptobenzothiazole by heating thiocarbanilide with sulfur under pressure. They also proposed a theory for the mechanism of the accelerating action as applied to thiocarbanilide and the thiazole derivatives.

The second paper of Bedford and Sebrell[5] revealed that the method of preparation described by Bruni and Romani had previously been known to them, and pointed out that the mechanism used by the latter workers to explain the action of thiocarbanilide as an accelerator was untenable.

The present investigation is a continuation of the work of Bedford and Sebrell. It has been carried out with the following purposes in mind:

1—To make a comparative study of the relative value of several derivatives of 1-mercaptobenzothiazole as accelerators of vulcanization.

2—By a process of substitution and elimination to determine what part of the mercaptobenzothiazole structure is responsible for the accelerating action of these compounds.

Preparation of Materials

1-Mercaptobenzothiazole and Its Derivatives—The preparation and properties of 1-mercaptobenzothiazole and its 3-methyl, 4-methyl, 5-methyl, 3,5-dimethyl, 5-methoxy, and 5-ethoxy derivatives have been fully described in Part I.

Other Benzothiazole Derivatives—In order to determine the particular grouping in the 1-mercaptobenzothiazole structure responsible for the accelerating action, it became necessary to prepare a series of related benzothiazole derivatives. In each case these compounds differed from the true 1-mercaptobenzothiazole by a single atom or grouping, the remaining part of the molecular structure being identical. All these substances have been previously described, but the details of their preparation are incomplete.

[1] Presented before the Division of Rubber Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

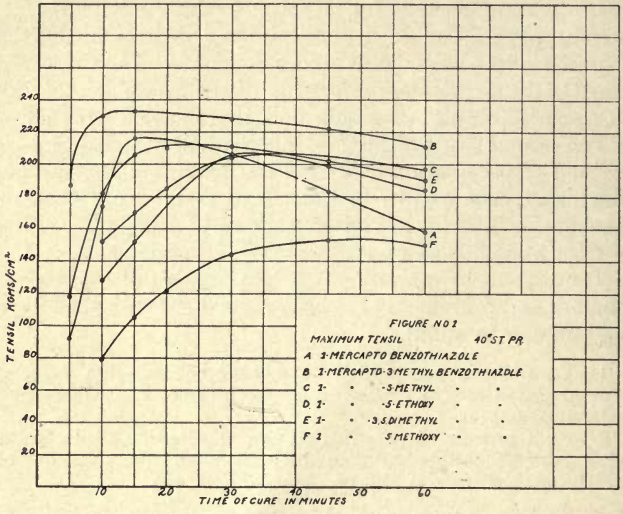
[2] *J. Ind. Eng. Chem.*, **15**, 1009.

[3] *Ibid.*, **13**, 1034 (1921).

[4] *Giorn. chim. ind. applicata*, **3**, 196 (1921).

[5] *Ind. Eng. Chem.*, **14**, 25 (1922).

1-Hydroxybenzothiazole,[6] $C_6H_4\begin{matrix}S\\ N\end{matrix}\!\!>\!COH$, was prepared by the hydrolysis of 1-chlorobenzothiazole, according to the method described by Hofmann.[6] Long heating of the free 1-chlorobenzothiazole does not accomplish the hydrolysis. However, if the hydrogen chloride addition product of 1-chlorobenzothiazole is heated with alcohol for 40 hours, the hydrolysis is almost complete. The solution was rendered strongly acid and precipitated by dilution with water. After two recrystallizations from 75 per cent alcohol 1-hydroxybenzothiazole was obtained as white needles melting at 136° C. This is the same melting point as given by Hofmann.



The hydrolysis of the hydrochloride may be accomplished in a much shorter time by heating with alcohol under pressure.

1-Amidobenzothiazole, $C_6H_4\begin{matrix}S\\ N\end{matrix}\!\!>\!C\!-\!NH_2$, was first prepared by Hofmann[7] by the action of alcoholic ammonia on 1-chlorobenzothiazole at 160° C. In this laboratory the method, as described, always yields the product in the form of a noncrystallizable sirup. Excellent results were obtained by the following method:

Fifteen grams of the 1-chlorobenzothiazole together with 45 cc. of saturated alcoholic ammonia and 15 cc. of aqueous ammonia were sealed in a tube and heated at 200° C. for 4 hours. On opening the tube the contents were mixed with 50 per cent alcohol, strongly cooled in an ice bath and diluted very slowly with water to 1 liter. After standing in an ice box for 12 hours 1-amidobenzothiazole was deposited as fine white needles, with only a trace of the sirupy impurity. The yield was 10 grams. This product after recrystallization from benzene melted at 127° C., compared with 129° C. recorded by Hofmann.

[6] *Ber.*, **12**, 1126 (1879); **13**, 9 (1880).
[7] *Ibid.*, **13**, 11 (1880).

1-Mercaptobenzoxazole, $C_6H_4\begin{smallmatrix}O\\ \diagup\diagdown\\ N\end{smallmatrix}CSH$, was prepared by refluxing an alcoholic solution of *o*-aminophenol with carbon disulfide according to the method of Dünner.[8] After the preliminary purification by precipitating from sodium carbonate solution, and recrystallization from water, the product melted at 193° C., the same as recorded by Dünner.

μ-Mercaptothiazolen, $\begin{smallmatrix}CH_2-S\\ |\quad\diagdown\\ CH_2-N\end{smallmatrix}CSH$, was prepared for the purpose of comparison with 1-mercaptobenzothiazole to determine the effect of the aromatic nucleus upon the accelerating power of the mercaptothiazoles. The compound was first described by Gabriel[9] who prepared it by the action of β-bromoethylamine hydrochloride and carbon disulfide in alkaline solution. Some difficulty was experienced in the isolation of both the hydrobromide and its reaction product with carbon disulfide, but a sufficient quantity was finally obtained to determine its relative value as an accelerator.

Results of Compounding Tests

All the compounds listed above were tested to ascertain their relative value as accelerators of vulcanization. The following experimental formula was used:

100.00 parts of rubber (smoked sheet)
5.00 parts of zinc oxide
3.50 parts of sulfur
1.00 part of 1-mercaptobenzothiazole or a molecular equivalent of its derivative or analog

With a few exceptions, each of these compounds produced very rapid curing in the formula given.

Since many of these substances are rapid and powerful accelerators, slight variations in the milling and curing may produce differences of some magnitude in the tensile-time diagrams. For this reason the conditions of milling and curing were standardized as follows:

The stocks were all mixed in 1-kg. batches on a small experimental mill. After milling for 20 minutes to break down the rubber, the zinc oxide and accelerator were added and mixed thoroughly into the stock for 10 minutes. The stock was then cooled to the lowest workable temperature and the sulfur added. After 5 minutes further mixing it was removed from the mill. All samples were milled as nearly as possible as described above.

The curing was conducted in a steam platen press in which the temperature was controlled as closely as possible. All cures were made in the same set of molds, which had been preheated before use by allowing them to remain for at least 30 minutes in the press at the required temperature. All the cures were made using the same decks of the same press. The vulcanized sheets after being removed from the molds were plunged into a tank of cold water to stop vulcanization.

[8] *Ber.*, **9**, 465 (1876); **16**, 1825 (1883).
[9] *Ibid.*, **21**, 566 (1888); **22**, 1137, 1152 (1889).

TABLE I—PHYSICAL TESTS—STOCKS CURED WITH MERCAPTOBENZOTHIAZOLES

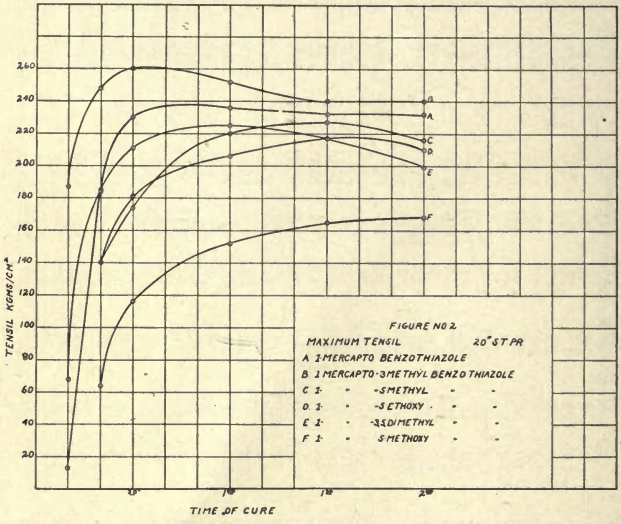
ACCELERATORS	Time of Cure Min.	100%	200%	300%	400%	500%	600%	700%	800%	Bk.	Elong.	Tensile Product	Energy of Resilience	STATE OF CURE
						40 pounds steam pressure (141° C.)								
1-Mercaptobenzothiazole	5	2.5	3	4	6	7	12	21	48	92	900	82.8	149.5	Under
	10	4	7	10.4	16	24	46	105	160	174	810	141.0	309	Best
	15	5	12	15	23	33	70	140	...	216	780	168.5	370	Slightly over
	30	4.5	8	13	20	36	75	150	...	206	780	161.0	374	Over
	45	5	9	12.5	21	34	66	125	...	183	770	141.0	318	Over
	60	5	9	12	19	34	55	114	...	158	770	121.7	286	Over
1-Mercapto-3-methylbenzothiazole	5	5	7	12	18	26	58	124	187	187	800	149.5	343	Slightly over
	10	7	10	17	25	43	85	167	...	230	780	179.5	330	Slightly over
	15	7	11	17	24	46	84	165	...	233	750	175.0	371	Over
	20	7	11	17	24	40	83	152	...	224	780	175	408	Over
	30	6	10	14	24	39	73	154	...	228	750	170	338.5	Over
	45	6	10	16	24	45	83	161	...	222	780	173	418	Over
	60	5	7	12	19	30	54	112	...	211	800	169	344	Over
1-Mercapto-5-methylbenzothiazole	10	4	5	7	12	15	27	65	122	152	860	131	278	Under
	15	4	6	8	12	19	36	82	151	170	830	141	290.6	Slightly under
	20	5	6	11	14	24	46	100	177	185	810	150	312.6	Very slightly over
	30	4	7	12	17	25	46	138	...	204	780	159	317	Very good over
	45	5	8	12	18	30	60	127	...	193	780	150.5	320.5	Over
	60	5	7	12	18	30	66	114	183	197	820	161	381.5	Over
1-Mercapto-5-ethoxybenzothiazole	10	4	6	8	12	17	28	58	99	128	850	109	239	Under
	15	4	6	11	15	24	44	95	149	157	815	128	296	Veryslightlyunder
	30	4	7	14	18	31	62	124	206	206	800	165	363	Over
	45	5	8	12	19	31	60	123	199	199	800	159	358	Over
	60	5	7	12	18	25	47	94	166	184	825	152	335	Over
1-Mercapto-5-methoxybenzothiazole	10	1	3	4	5	7	12	19	$36\frac{900}{72}$	79	975	105	179.6	Under
	15	3	4	6	7	12	18	36	66	106	900	94.5	204	Under
	20	4	5	7	10	15	24	47	90	121	860	104	220	Under
	30	4	6	10	12	23	42	83	...	144	780	112	230	Under
	45	3	6	9	14	20	34	69	132	153	860	132	306.5	Fair
	60	4	6	10	12	22	40	78	144	150	820	123	273	Good
1-Mercapto-3-5-dimethylbenzothiazole	5	3	4	6	7	11	18	32	74	118	890	105	204	Under
	10	5	6	11	16	23	46	108	172	182	810	143	319	Very slightly over
	15	4	6	11	17	25	50	120	206	206	800	165	336	Over
	20	5	9	14	23	39	77	142	...	210	780	164	379	Over
	30	5	10	13	21	38	77	149	211	211	800	169	419	Over
	45	5	7	12	18	30	54	113	178	202	825	167	375.5	Over
	60	6	7	12	19	30	59	108	...	190	790	150	321	Over

20 pounds steam pressure (125° C.)

1-Mercaptobenzothiazole	10	1	2	3	4	5	6	8	12	13	820	10.7	60	Under
	20	4	6	10	15	21	41	78	152	184	845	155	326.6	Slightly under
	30	5	8	14	20	31	68	135	230	230	800	184	401	Best
	60	5	10	16	24	44	90	174	...	236	760	179	399	Over
	90	5	10	16	25	44	92	174	...	232	770	178	421	Much over
	120	5	10	17	25	46	87	173	...	232	770	178	417	Much over
1-Mercapto-3-methylbenzothiazole	10	4	8	10	16	22	41	89	168	187	830	155	318	Slightly under
	20	5	10	16	24	40	75	146	...	248	790	196	320	Slightly over
	30	6	12	19	29	50	103	205	...	260	750	195	437	Over
	60	6	11	19	31	54	110	214	...	252	740	187	431	Over
	90	6	14	20	30	50	110	216	...	240	730	175	406	Much over
	120	6	14	20	30	54	110	187	...	240	730	175	391	Much over
1-Mercapto-5-methylbenzothiazole	20	3	5	8	10	15	26	47	93	140	900	126	277	Under
	30	5	8	10	15	25	48	99	174	174	800	139	337	Under
	60	5	10	16	21	33	76	144	...	220	790	166	397	Good, slightly over
	90	5	10	15	24	38	74	150	...	227	790	172	410	Over
	120	5	10	15	25	42	76	166	...	213	760	162	369	Over
1-Mercapto-5-ethoxybenzothiazole	20	3	5	8	10	15	26	50	101	140	890	125	276	Under
	30	5	6	10	14.5	21	35	75	146	182	860	157	338	Slightly under
	60	5	10	12	20	31	62	135	...	195	770	150	323	Best
	90	5	10	15	22	35	71	134	...	218	770	168	348	Over
	120	5	10	15	24	41	85	152	...	210	780	164	401	Over
1-Mercapto-5-methoxybenzothiazole	20	2	3	4	5	6	10	16	25	64	980	62.7	139	Very much under
	30	3	4	5	8	12	21	40	72	116	900	105	223	Much under
	60	5	7	10	15	21	36	78	136	142	830	118	282	Fair
	90	4	6	10	16	25	46	93	...	165	800	132	283	Fair
	120	5	9	15	20	30	54	108	...	168	780	131	297	Best
1-Mercapto-3-5-dimethylbenzothiazole	10	2	3	4	5	7	11	18	34	68	940	64	136	Under
	20	4	8	12	17	25	56	112	...	185	790	146	312	Good, slightly under
	30	6	10	15	21	36	74	153	...	211	765	162	475	Good, slightly over
	60	5	10	16	26	46	102	200	...	225	740	167	390	Over
	90	5	10	18	27	48	98	185	...	194	720	140	336	Much over
	120	5	10	16	26	46	92	183	...	199	740	147	363	Much over

The physical data given in the following tables were obtained by two observers on a Scott testing machine using dumb-bell test pieces. The average of two or more closely agreeing strips is given for each cure.

The results of the physical tests on the cures made with 1-mercaptobenzothiazole, its alkyl and alkyloxy derivatives, are recorded in Table I, and are represented graphically in Figs. 1 and 2. In comparing the relative activity of these compounds, the writers have used as a basis of comparison the time in which each compound was judged to give the best technical cure. This can best be determined by subjecting the stocks themselves to certain arbitrary tests, such as the effect of repeated flexing and resistance to tear. The nature of the grain as indicated by the appearance of the tear is also



taken into consideration. The results of such tests are given for each cure in the tables in the column "State of Cure." In some cases the cures were not sufficiently close so that, for example, a 5-minute cure might be judged by means of these tests to be undercured, while a 10-minute cure would be considerably overcured. In such cases the writers have interpolated for the time of best technical cure.

The relative order of activity of these compounds as accelerators cannot well be determined from a comparison of the maximum tensiles obtained, since the test sheet which would give the highest tensile is in almost all cases overcured from a practical standpoint. Any attempt to classify the compounds on the basis of the so-called optimum cure, as given by either the maximum tensile product or the energy of resilience, or a combination of these factors, would be subject to the same objection as given above for the classification in order of maximum tensile.

If it is desired to utilize the stress-strain data in determining the relative activity of these compounds, they can, for example, be ranked in the order of the highest tensile stress at 700 per cent elongation given by a 10-minute cure on each compound at 40 pounds steam pressure. In this way the errors inherent in a determination of the maximum tensile are avoided. If such a classification is made it will be found that the compounds arrange themselves in exactly the same order as determined by the best technical cure.

The writers are therefore inclined to classify the various mercaptobenzothiazoles according to the time necessary to produce the best cure from a practical standpoint as shown by the above arbitrary tests, and to use the stress-strain data as a measure of the quality of the stocks.

It is realized that the present method of determining the relative activity might not seem satisfactory to all, and for this reason the complete data for the physical tests, together with the tensile product and the energy of resilience, have been included in the tables.

Since only one formula was used in testing all these accelerators and because in some cases an insufficient number of cures have been obtained, it is obvious that the results herein presented cannot be considered as representing a complete or detailed compounding investigation. They are, however, considered satisfactory from the standpoint of determining the relative activity of the various mercaptobenzothiazoles and their derivatives as accelerators.

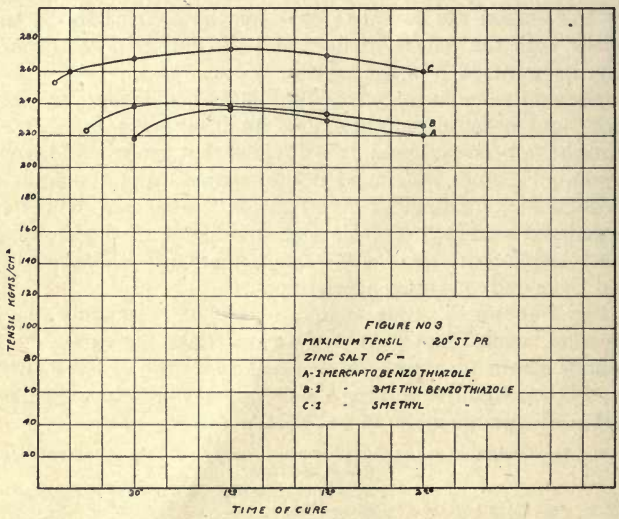
Fig. 1 shows the tests made on cures at 40 pounds steam pressure, while Fig. 2 gives the same data for cures at 20 pounds steam pressure. The relative activity of the 1-mercaptobenzothiazoles and the time required to produce the best technical cure are given in Table II.

TABLE II.—ORDER OF REACTIVITY OF THE 1-MERCAPTOBENZOTHIAZOLES AS ACCELERATORS

SUBSTANCE	40 Pounds Pressure		20 Pounds Pressure	
	Time of Best Technical Cure	Order of Activity	Time of Best Technical Cure	Order of Activity
1 - Mercapto - 3 - methylbenzothiazole.....	5 min.	1	18 min.	1
1 - Mercapto - 3,5 - dimethylbenzothiazole...	8 min.	2	25 min.	2
1-Mercaptobenzothiazole.	10 min.	3	30 min.	3
1 - Mercapto - 5 - methylbenzothiazole.....	18 min.	4	55 min.	4
1 - Mercapto - 5 - ethoxybenzothiazole.....	20 min.	5	60 min.	5
1 - Mercapto - 5-methoxybenzothiazole.....	1 hr.	6	2 hrs.	6

The data showing the relative curing power of 1-mercapto-4-methylbenzothiazole are not given in Table II. A limited supply of this material prevented it from being included when the foregoing tests were made. It had previously been tested in a different formula. Under these conditions its activity as an accelerator was found to lie between the 5-methyl and 3-methyl derivatives, being very close to that of 1-mercaptobenzothiazole.

In the absence of zinc oxide the 1-mercaptobenzothiazoles are without appreciable accelerating action. Compounded in the foregoing formula, except that the zinc oxide was omitted, 1-mercaptobenzothiazole cured at 40 pounds steam pressure for 2 hours gave a maximum tensile strength of 96 kg. per sq. cm. Curing the same mixture at 20 pounds steam pressure for the same time gave a maximum tensile strength of 50 kg. per sq. cm. These substances, therefore, have no practical value as accelerators except in the presence of zinc or lead oxides. From these results it seems probable that in the process of vulcanization the mercaptobenzothiazoles are converted into the corresponding zinc salts, these salts acting as the true accelerating agents. To test this assumption the zinc and lead salts of 1-mercapto-, 1-mercapto-3-methyl, and 1-mercapto-5-methylbenzothiazoles were tested in the foregoing



formula. The results are shown in Tables III*a* and III*b* and the tensile–time curves in Figs. 3 and 4.

The zinc salt of the 5-methyl derivative is slightly faster in its curing action than the zinc salt of the free 1-mercaptobenzothiazole or its 3-methyl derivative. The last two are about equal in curing power. On the other hand, the lead salt of the 3-methyl derivative is the most active of the three lead salts, giving good cures in 15 minutes at 20 pounds steam pressure. The two remaining lead salts are about equal in activity but vary in the tensile strengths produced.

In all cases the zinc and lead salts of these mercaptobenzothiazoles are much more powerful accelerators than the corresponding free compounds. The zinc salt is, generally, more powerful than the corresponding lead salt. These metallic salts must also be used with additional metallic oxide to obtain their maximum accelerating power.

TABLE III*a*—PHYSICAL TESTS: STOCKS CURED WITH THE ZINC SALTS OF MERCAPTOBENZOTHIAZOLE

20 pounds steam pressure (125° C.)

ACCELERATOR	Time of Cure Min.	100%	200%	300%	400%	500%	600%	700%	800%	Bk.	Elong.	Tensile Product	Energy of Resilience	STATE OF CURE
1-Mercaptobenzothiazole	30	8	13	20	29	52	109	202	...	218	720	155	374	Over
	60	8	14	22	36	64	127	221	...	236	715	169	415.8	Over
	90	9	14	23	39	67	130	219	...	229	715	163	425	Over
	120	9	14	23	37	64	125	206	...	220	720	158	417.6	Over
	180	8	14	21	33	55	106	188	...	210	720	151	370.8	Over
1-Mercapto-3-methylbenzothiazole	15	6	10	15	39	53	104	198	...	223	750	167	431	Good
	30	6	11	21	38	73	141	219	...	238	740	167	490.9	Over
	60	6	12	21	36	62	120	218	...	238	730	174	434.4	Over
	120	6	12	18	32	57	108	200	...	226	740	167.5	418	Over
	180	6	12	19	33	57	107	190	...	220	740	163	493	Over
1-Mercapto-5-methylbenzothiazole	5	5	9	13	21	37	67	133	220	253	825	204	454	Slightly under
	10	5	9	13	22	40	80	142	...	260	855	222	350.5	Under
	30	6	10	18	26	52	102	183	...	268	850	228	418	Over
	60	6	12	20	30	60	114	208	...	274	745	204	454	Over
	120	6	13	20	34	62	114	211	...	260	730	190	425	Over
	180	5	10	20	32	60	104	185	...	238	760	181	450.4	Over

TABLE III*b*—PHYSICAL TESTS: STOCKS CURED WITH NORMAL LEAD SALTS OF MERCAPTOBENZOTHIAZOLES

20 pounds steam pressure (125° C.)

ACCELERATOR	Time of Cure Min.	100%	200%	300%	400%	500%	600%	700%	800%	Bk.	Elong.	Tensile Product	Energy of Resilience	STATE OF CURE
1-Mercaptobenzothiazole	15	7	8	12	18	30	58	108	...	142	760	108	232	Good
	30	6	11	16	25	42	78	145	...	181	740	134	315.7	Over
	60	7	12	18	39	46	97	165	...	202	710	144	319.8	Over
	90	6	11	18	39	46	86	160	...	206	750	155	377.5	Over
	120	6	11	17	27	24	81	141	...	202	760	154	339.4	Over
	180	7	10	15	25	40	70	129	...	183	780	143	356	Over
1-Mercapto-3-methylbenzothiazole	15	5	9	16	26	45	92	162	250	260	835	217	551	Good
	30	5	9	17	27	46	97	175	...	255	752	192	400	Over
	60	7	11	17	28	48	102	186	...	248	785	193	490.5	Over
	120	6	12	19	29	50	105	190	...	241	745	179	413	Over
	180	6	10	20	30	54	106	186	...	238	767	182	461	Over
1-Mercapto-5-methylbenzothiazole	10	3	5	7	9	10	18	36	60 $\frac{900}{100}$	113	960	108.5	261.9	Under
	25	5	9	14	20	25	60	120	...	180	790	142	328	Good
	60	5	10	16	26	41	88	164	...	225	760	171	384.7	Over
	120	5	10	15	25	49	92	171	...	226	770	169	420	Over
	180	5	10	16	35	45	79	158	...	220	800	716	458	Over

The disulfides of the several mercaptobenzothiazoles were also tested in the foregoing formula, and were found to be considerably less active than the free thiazoles.

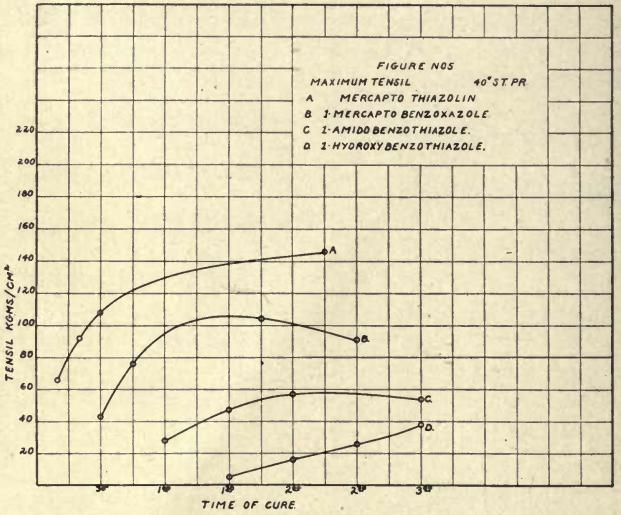
Two conclusions may be drawn from these facts:

1—The 1-mercaptobenzothiazoles when used as accelerators first form the metallic salts by action with the metallic oxide present. These salts are the active accelerators.

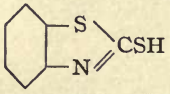
2—The salts so formed tend to decompose during the process of vulcanization and an excess of the metallic oxide must be present to reform the salts and thus maintain the accelerating action

Tests on Compounds Similar to 1-Mercaptobenzothiazole

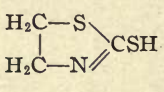
μ-Mercaptothiazoline (*A*), 1-mercaptobenzoxazole (*B*), 1-amidobenzothiazole (*C*), and 1-hydroxybenzothiazole (*D*) were also tested for their accelerating action Each of these



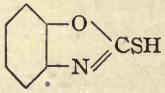
compounds resembles 1-mercaptobenzothiazole in certain parts of its structure. The results of these tests are recorded in Table IV and shown graphically in Fig. 5.



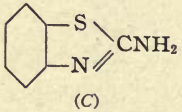
1-Mercaptobenzothiazole



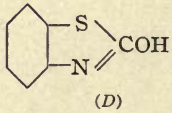
(*A*)



(*B*)



(*C*)

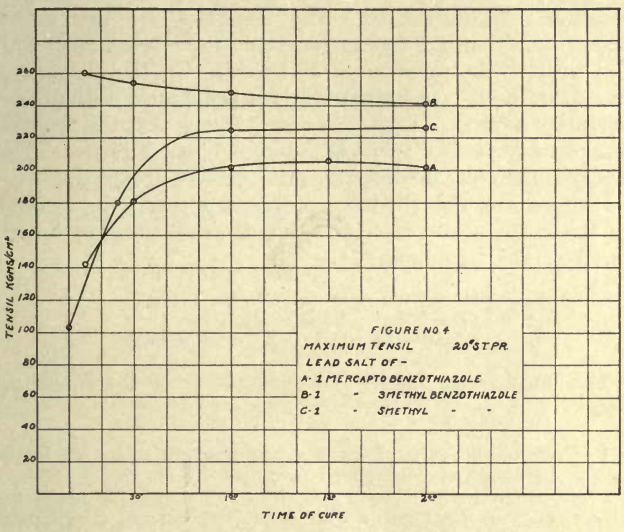


(*D*)

The results show that the μ-mercaptothiazoline exerts a marked accelerating action, but much less than that of 1-

mercaptobenzothiazole. This would seem to indicate that the accelerating power is invested in the mercaptothiazole group. When the sulfur atom of the thiazole ring is replaced by oxygen as in 1-mercaptobenzoxazole, the accelerating action is still evident but much lower than that of either 1-mercaptobenzothiazole or μ-mercaptothiazoline.

If the mercapto group is replaced by an amino or an hydroxyl group, as in 1-amidobenzothiazole or 1-hydroxybenzothiazole, respectively, the accelerating action is very greatly



diminished; indeed, in the latter substance it is almost entirely absent.

The conclusions to be drawn from these results are as follows:

1—The accelerating action of 1-mercaptobenzothiazole and its derivatives is invested primarily in the mercaptothiazole group. The presence of the benzene nucleus adds markedly to the accelerating value. Whether this is due to the attendant increase in the molecular weight or more directly concerned with the chemical characteristics of the benzene nucleus, is not yet determined.

2—The atomic grouping,  , is directly responsible for the accelerating action. Any change in this grouping either greatly diminishes or completely destroys the accelerating value.

3—The mercapto group is more essential to the acceleration than the sulfur of the thiazole ring, although both are necessary to the best results.

Mechanism of Acceleration by Mercaptobenzothiazole Derivatives

Several theories have recently been advanced to explain the vulcanization of rubber by organic compounds containing

the mercapto group. Bruni and Romani[5] have proposed the following mechanism for the acceleration of vulcanization by mercaptobenzothiazoles:

$$2R{-}SH + ZnO \longrightarrow (R{-}S)_2Zn + H_2O$$
$$x(R{-}S)_2Zn + Sx \longrightarrow xR{-}S{-}S{-}R + xZnS$$
$$R{-}S{-}S{-}R \longrightarrow R{-}S{-}R + S \ (\textit{active})$$

They have lately extended this theory to many other well-known accelerators, such as thiocarbanilide and aldehyde ammonia.[11] It is chiefly interesting as it applies to mercaptobenzothiazole derivatives. The disulfides are less active accelerators than the free mercaptobenzothiazoles, both with and without the presence of zinc oxide. In the absence of zinc oxide both types of derivatives are almost without accelerating power. These facts seem to show that the disulfide cannot be the active agent in this type of acceleration. The theory is therefore inadequate and cannot be accepted.

Bedford and Sebrell[6] have proposed a theory to account for the action of mercapto compounds as accelerators, which may be stated as follows:

$$2R{-}SH + ZnO \longrightarrow (R{-}S)_2Zn + H_2O$$
$$(R{-}S)_2Zn + S_x \longrightarrow (R{-}SS_x)_2Zn$$
$$(R{-}SS_x)_2Zn \longrightarrow (R{-}S)_2Zn + S \ (\textit{active})$$

This mechanism affords an explanation of the following facts:

1—The metallic salts of the mercaptobenzothiazoles are faster curing than the free compounds.

2—Both the metallic salts and the free compounds are faster curing than the disulfides, which must first undergo a reduction to the mercaptans before functioning as accelerators.

3—All mercaptobenzothiazoles require the presence of zinc or lead oxides for the development of full accelerating power.

4—The metallic salt of the mercaptan is therefore assumed to be the active agent. Excess metallic oxide must be present at all times to reform the salt if it should be decomposed by the action of heat or hydrogen sulfide. Evidence of such decomposition is to be found in the low curing power of these salts in the absence of metallic oxides, and their superior power when an excess of the oxide is present.

While it cannot be shown that sulfur split off from polysulfides is an active form, it has been proven that the sulfur in trithioozone is particularly active,[6] and it is inferred that the sulfur yielded by the decomposition of the polysulfides is similarly active.

The polysulfide theory, as given above, appears to offer the best explanation of the existing facts. Doubtless, both the mechanisms given above function in specific cases. It is also probable that no simple explanation of activation will be found which is equally applicable to all types of accelerators. Further work is being done to determine the validity of each of the reactions involved in the above mechanisms.

[11] Romani, *Caoutchouc gutta-percha*, **19**, 11626 (1922).

TABLE IV—PHYSICAL TESTS: STOCKS CURED WITH ANALOGS OF MERCAPTOBENZOTHIAZOLE

40 pounds steam pressure (141° C.)

ACCELERATOR	Time of Cure Min.	100%	200%	300%	400%	500%	600%	700%	800%	Bk.	Elong.	Tensile Product	Energy of Resilience	STATE OF CURE
μ-Mercaptothiazoline	10	1	2	4	6	8.5	10	20	34	66	900	59.4	68.5	Under
	20	3	4.5	6	9	14	19	35	66	92	895	82.3	197.5	Under
	30	2.5	5	6.5	9	14	23	45	85	108	870	94.0	215	Fair
	45	3.5	5	8	10	14	24	50	95	109	845	92	207.9	Fair
	60	3.5	5	8	11	16	28	48	96	104	825	86	192.5	Slightly over
	135	4	7.5	11	15	23	41	86	..	138	785	108	239.7	Over
1-Mercaptobenzoxazole	30	2	2.5	3.5	4.5	5.5	7	9	14	43	990	42.5	66.6	Under
	45	2	3	5	5.5	7	10	18	32	76	995	75.5	117.8	Under
	60	2.5	4	5	6	10	14	26	42	81	960	77.5	125.4	Under
	105	3	5	6.5	9	12	19	31	59	104	910	94.5	205.8	...
	150	3.5	5	8	10	14	21.5	35	68	91	875	75	190.6	...
1-Amidobenzothiazole	60	2	2.5	3	4.5	6	9	14	22	28	870	24	69.5	All cures poor
	90	1.5	2.5	4	5	8	11	18	28	46	880	40	93.6	
	120	2.5	3.5	5	8	10	17	27	50	57	825	47	111.4	
	180	2.5	4	5.5	9	14	23	38	..	54	785	42.5	116.1	
1-Hydroxybenzothiazole	90	0.5	1	1.5	2	3	4	..	..	5	620	3	10.9	No cures
	120	1	2	3	4	4.5	6	9	14	16	840	13.5	42.5	
	150	0.5	1.5	2.5	3.5	4.5	6	10	17	26	880	23	54.2	
	180	1.5	2	3	5	8	10	18	30	38	850	32	79.5	

SUMMARY

Mercaptobenzothiazole and its substituted derivatives show the following relative activity as accelerators of vulcanization: (1) 3-methyl, (2) 3,5-dimethyl, (3) unsubstituted, (4) 4-methyl, (5) 5-methyl, (6) 5-ethoxy, (7) 5-methoxy. Several compounds with a structure analogous to 1-mercaptobenzothiazole were prepared and their accelerating values determined. The mercaptobenzothiazoles have no value as accelerators except in the presence of zinc oxide. The zinc and normal lead salts of these thiazoles are faster curing than the corresponding free thiazoles. The zinc salt of the 1-mercapto-5-methylbenzothiazole and the normal lead salt of 1-mercapto-3-methylbenzothiazole gave the highest accelerating values of any of the compounds tested. The disulfides have a lower curing power than the corresponding free thiazoles. The accelerating power of the mercaptobenzothiazoles is directly connected with the atomic grouping $-S-\overset{\|}{C}-SH$. Any alteration in this grouping removes almost entirely the power to accelerate rubber vulcanization. The mercapto group is more essential to the accelerating action than the sulfur atom of the thiazole ring. Both are necessary to develop the highest accelerating power. Aliphatic mercapthiazoles show marked accelerating power but are inferior to the mercaptobenzothiazoles. The metallic salts of the mercaptobenzothiazoles are assumed to be the active agents in producing acceleration.

The existing theories for the mechanism of acceleration by mercapto compounds have been given. The results obtained in the work are correlated with the polysulfide theory.

ACKNOWLEDGMENT

The writer wishes to acknowledge his indebtedness to Dr. C. E. Boord under whose direction this work has been carried out. His unfailing courtesy and optimistic spirit have been manifest at all times; and his helpful and kindly advice has helped to make the research a real pleasure.

The writer also wishes to acknowledge the coöperation of the Goodyear Tire and Rubber Company, as expressed through Dr. E. B. Spear, for the loan of apparatus and the testing of samples. Further acknowledgment is due Mr. C. W. Bedford and Dr. W. J. Kelly for valued suggestions, and to Mr. C. M. Carson for assistance rendered.

AUTOBIOGRAPHY

I, Lorin Beryl Sebrell, was born at Alliance, Ohio, November 19, 1894. My elementary and secondary education was received in the public schools and high school of that city, and my undergraduate college training at Mt. Union College. I received the Bachelor of Science degree from the same institution in 1916, and in 1917, I was granted the degree of Master of Science by the Ohio State University. During the war I was connected with the Research Division of the Chemical Welfare Service. After the war I served one year as instructor in chemistry at Case School of Applied Science. In 1919 I entered the employ of the Goodyear Tire and Rubber Company as a research chemist, holding this position until February, 1921, when I left to resume graduate work at the University of Wisconsin. I returned to the Ohio State University in January, 1922, and completed the requirements for the degree of Doctor of Philosophy at the end of the summer quarter, 1922.