

## Room Temperature Sulfur and Nonsulfur Vulcanization of Natural Rubber: with Sulfur and Piperidinium *N*-Pentamethylenedithiocarbamate and with Quinone Dioxime (GMF) and Yellow Mercuric Oxide

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### I. VULCANIZATION WITH SULFUR AND PIPERIDINIUM *N*-PENTAMETHYLENEDITHIOCARBAMATE

Room temperature or cold vulcanization has been carried out in several different ways, chiefly through the use of ultra-accelerators. Mention should be made, however, of the use of active forms of sulfur without the aid of ultra-accelerators. Peachey<sup>1</sup> showed that a thin sheet of raw rubber is vulcanized by exposing it at room temperature for 10 min. to sulfur dioxide gas and then for 30 min. to hydrogen sulfide gas, and that it then contains upwards of 2.5% of combined sulfur. The same gases can also be used to vulcanize raw rubber in solution without the application of heat. Furthermore, Bedford and Sebrell<sup>2</sup> record an experiment in which the sulfur formed by the action of these same two gases in benzene at 10°C. vulcanized rubber in solution at a temperature below that of the room. These researchers also found<sup>3</sup> that cements could be vulcanized at room temperature by the action of ordinary sulfur in the presence of an ultra-accelerator (aniline + CS<sub>2</sub>) and zinc oxide. The combined sulfur values ranged from 0.53 to 1.06, based on 100 parts of rubber used. The same method was discovered independently by Bruni.<sup>4</sup>

Cold vulcanization with an ultra-accelerator was first described by Ostromyslenskiĭ<sup>5</sup> in 1915. He states that if 2.5 g. sulfur and 0.5 g. piperidinium *N*-pentamethylenedithiocarbamate are milled into 50 g. "Peruvian rubber" at 140–158°F. for 25–35 min. until the mass is uniform, and kept in a mold at ordinary temperature for 5 days, vulcanization is complete. A sample thus vulcanized contained 2.97% combined sulfur, had a tensile strength of 19 kg./cm.<sup>2</sup> (270 lb./in.<sup>2</sup>)—a strength which is very low—and exhibited 6.5–7 fold elongation. Addition of zinc oxide gave a much "better"

reaction, but no specific test results are given. Ostromyslenskiĭ also mentions mixing the rubber in small batches in the cold and allowing them to stand for 2–6 months. In the example given above, we think that vulcanization would not have taken place so rapidly if the mixture had not been milled rather long at a temperature above that of the room.

Cranor<sup>6</sup> also mixed an ultra-accelerator, sulfur, and zinc oxide into rubber on a mill, calendered the mixture, and set it aside between Holland cloth to vulcanize at room temperature (70–90°F.). The mixture consisted of 100 parts of smoked sheet, 6 parts sulfur, 1 part zinc oxide and 1 part dimethylammonium *N*-dimethyldithiocarbamate, and the results of physical tests, made with and across the grain, and of analysis for sulfur are given in Table I.

Some heat is always generated when rubber is rolled to render it plastic on a mill, and therefore a batch containing an ultra-accelerator is very likely to undergo a premature vulcanization known as "scorching." In order to avoid the possibility of scorching, various methods have been used to introduce the ultra-accelerator and sulfur into the rubber without the use of a mill. In general these are as follows.

1. The rubber mixture is made without sulfur, and powdered sulfur then dusted on the surface.

TABLE I

Vulcanization time	Direction of test	Tensile strength, kg./cm. <sup>2</sup> , psi	Elongation, %	Vulcaniz. coeff. <sup>a</sup>
33 days	With grain	146.9(2090)	840	0.77
33 days	Across grain	161.0(2290)	940	0.77
2 mos.	With grain	172.8(2458)	850	1.05
2 mos.	Across grain	159.3(2266)	860	1.05

<sup>a</sup> Coefficient of vulcanization is in terms of parts sulfur incorporated per 100 parts rubber.

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Sulfur is soluble in rubber and penetrates very readily. This process is due to Pestalozza,<sup>7</sup> who states that it was in commercial use in 1918.

2. The materials may be mixed into a solution of rubber and the solvent allowed to evaporate, or the mixture allowed to vulcanize in the solution and the solvent then evaporated.<sup>4</sup>

3. The accelerator may be prepared in the rubber mixture, for example, by milling in an amine, such as aniline or dibenzylamine, and applying carbon disulfide as a liquid or vapor to the surface.<sup>4,8,9</sup>

4. Alternate plies of thin sheets of rubber mixtures, one of which contains the sulfur and the other the ultra-accelerator, are so arranged that these materials may migrate from one to the other layer;<sup>10</sup> alternatively, each layer may contain a substance which is not an ultra-accelerator in itself but diffuses and combines chemically with the other substance to form an ultra-accelerator, for example, *O*-ethyl thiocarbonic acid disulfide (Dixanthogen) and aniline.<sup>9</sup>

5. The rubber mixture may be soaked in a solution of an ultra-accelerator, or the ultra-accelerator may be dusted upon the rubber mixture.<sup>11</sup>

In none of the above cases does there seem to have been any physical or chemical data published on rubber vulcanized at room temperature. This was done in the present instance on samples which had no heat applied on the rubber-sulfur mix.

In the present work Pestalozza's method (1) of dusting the rubber mixture with sulfur was used. These mixtures vulcanize completely in 15 min. in boiling water or in several weeks on standing at room temperature. We believe the results show that the chemical combination of sulfur with the rubber hydrocarbon goes on from the time the sulfur and accelerator come in contact with the rubber hydrocarbon, and, in the presence of an excess of sulfur, continues without reaching a maximum, even up to 115 weeks.

### Experimental

A mixture was made up on a laboratory mill consisting of 100 parts pale crepe, 2 parts zinc oxide, and 2 parts piperidinium *N*-pentamethylenedithiocarbamate and the mix calendered to 1.57 mm. (0.062 in.). Sheet specimens, 76.2 × 101.6 mm. (3 × 4 in.), embedded in powdered sulfur at room temperature, were set aside. Periodically a sheet specimen was removed, tested for tensile strength and elongation, usually both with and across the grain, and analyzed for combined sulfur. Com-

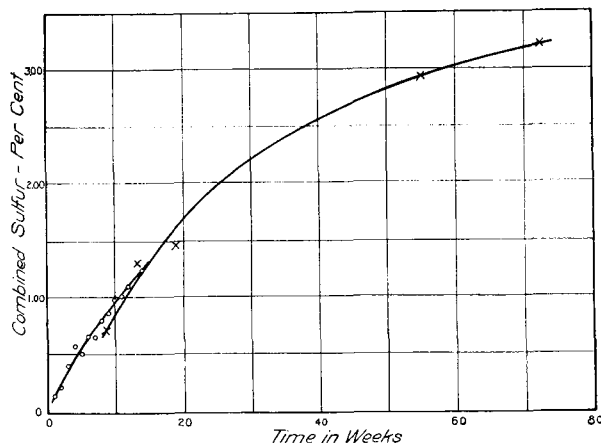


Fig. 1. Plot of combined sulfur in sample vs. vulcanization time: (X) series 1; (O) series 2.

parative analyses for combined sulfur were made for some samples by cold extraction with acetone as well as by the usual hot extraction. The cold extraction was done in order to avoid entirely the action of heat on the samples. The two methods gave identical results, within the experimental error, and, therefore, practically all subsequent analyses were by hot extraction.

Two sheet specimens which were not embedded in sulfur were analyzed at the end of 8½ weeks by both cold and the hot extraction methods; these samples showed only 0.01 and 0.03% for combined sulfur, respectively. The amount of sulfur in the ultra-accelerator used corresponded to 0.52% of the total mixture.

Two series of the same mixture were made. The sheet specimens in the first series were allowed to

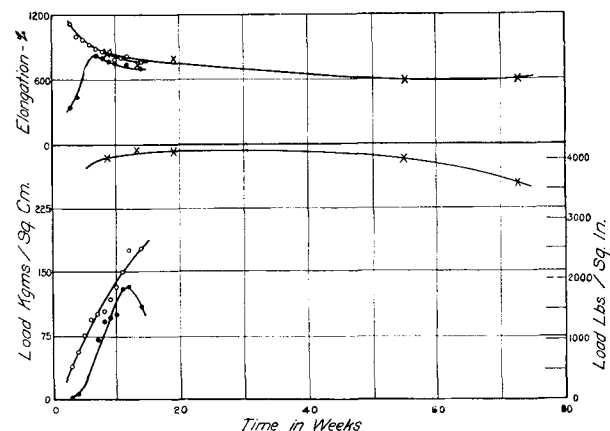


Fig. 2. Plot of vulcanization time vs. (top) elongation and (bottom) tensile strength of vulcanizates: (X) series 1, with grain; (O) series 2, with grain; (●) series 2, against grain.

remain undisturbed for two months before any tests were made. The first specimen removed showed a tensile strength of 284.0 kg./cm.<sup>2</sup> (4040 psi) and, therefore, a second series was started later in order to obtain data up to this particular time. The tensile strengths were greater in the first series than in the second, the difference probably being due to a difference in the original rubbers used and in the handling during milling and calendering. The amounts of combined sulfur are approximately the same in both series, since the rate of combination is not affected by the amount of milling.<sup>12</sup>

The experimental results are shown in the accompanying curves (Figs. 1 and 2). Figure 1 shows the amount of combined sulfur in the specimens in each series; Figure 2 gives the tensile strengths and elongations in each series. In series 1, only the results with the grain are given. The high tensile strengths in series 1, i.e., 284.0 to 294.2 kg./cm.<sup>2</sup> (4040–4185 psi) are worthy of note, especially when it is considered that no heat at all was used. The first sample tested in series 1 with the high tensile strength contained only 0.73% combined sulfur. In series 2, the combined sulfur at the end of the first week was 0.15%; at the end of the second week, 0.22; and at the end of the third week, 0.39; the tensile strength of this first sample was 50.6 kg./cm.<sup>2</sup> (720 psi). The remaining sample of series 1 was tested at the end of 115 weeks, with the following results: tensile strength 239.7 kg./cm.<sup>2</sup> (3410 psi) and elongation 530% with the grain; tensile strength 196.1 kg./cm.<sup>2</sup> (2790 psi) and elongation 490% across the grain; combined sulfur, 3.60%. These latter results are not shown on the curves.

## II. VULCANIZATION WITH QUINONE DIOXIME (GMF) AND YELLOW MERCURIC OXIDE

Quinone dioxime (GMF)<sup>13</sup> and certain oxidizing agents in rubber vulcanize the rubber when

heated. Since they sometimes scorch on the mill and the mixture sets up on standing, an experiment was therefore carried out to determine the extent of vulcanization, if any, at room temperature. The plan was to mix the oxidizing agent into rubber, calender the mix, and let it stand covered with quinone dioxime. Mercuric oxide was chosen as the oxidizing agent since it is not a pro-oxygen; in other words, it does not cause rubber to become sticky on standing in the air.

Quinone dioxime (GMF) penetrates a thin, calendered, pale crepe rubber mix containing yellow mercuric oxide and vulcanization takes place at room temperature. Once a certain reaction has occurred, the physical properties of the vulcanizate remain unchanged for an unknown period of time. The tensile strength developed is almost as high as that obtained in a press cure with quinone dioxime alone. With 3 parts quinone dioxime in 100 parts of pale crepe at 141°C. (286°F.) a tensile strength of kg./cm.<sup>2</sup> (290 psi) was attained in 30 min.; with the same mix the tensile strength was 69.7 kg./cm.<sup>2</sup> (991 psi) in 120 min. With 10 parts quinone dioxime the tensile strengths were 58.7 kg./cm.<sup>2</sup> (835 psi) and 75.2 kg./cm.<sup>2</sup> (1070 psi) after 30 and 120 min., respectively.

The untreated, calendered pale-crepe rubber-mercuric oxide mix with no quinone dioxime initially shows a certain set, probably a regaining of nerve; this condition then remains unchanged. The low set and low stretch obtained after 405 days was probably due to poor breaks in the samples tested. When heated to 141°C. (286°F.), a mix of 40 parts (3.6 volumes) yellow mercuric oxide in 100 parts pale crepe gives a good vulcanizate with a tensile strength of 35.2 kg./cm.<sup>2</sup> (500 psi); a mixture containing 120 parts (10.8 volumes) gives vulcanizate with a tensile strength of 73.1 kg./cm.<sup>2</sup> (1040 psi).

When calendered pale crepe was set aside in

TABLE II

Vulcanization time, days	Rubber + yellow mercuric oxide embedded in quinone dioxime				Rubber + yellow mercuric oxide only			
	Tensile strength, kg./cm. <sup>2</sup>	(psi)	Set	Elongation, %	Tensile strength, kg./cm. <sup>2</sup>	(psi)	Set	Elongation, %
11	No signs of vulcanization				No signs of vulcanization			
49	No signs of vulcanization				No signs of vulcanization			
181	27.5	(393)	—	720	5.3	(76)	—	730
405	52.8	(754)	0.16	840	5.3	(75)	0.06	230
930	53.6	(763)	0.16	850	4.9	(69)	0.28	920

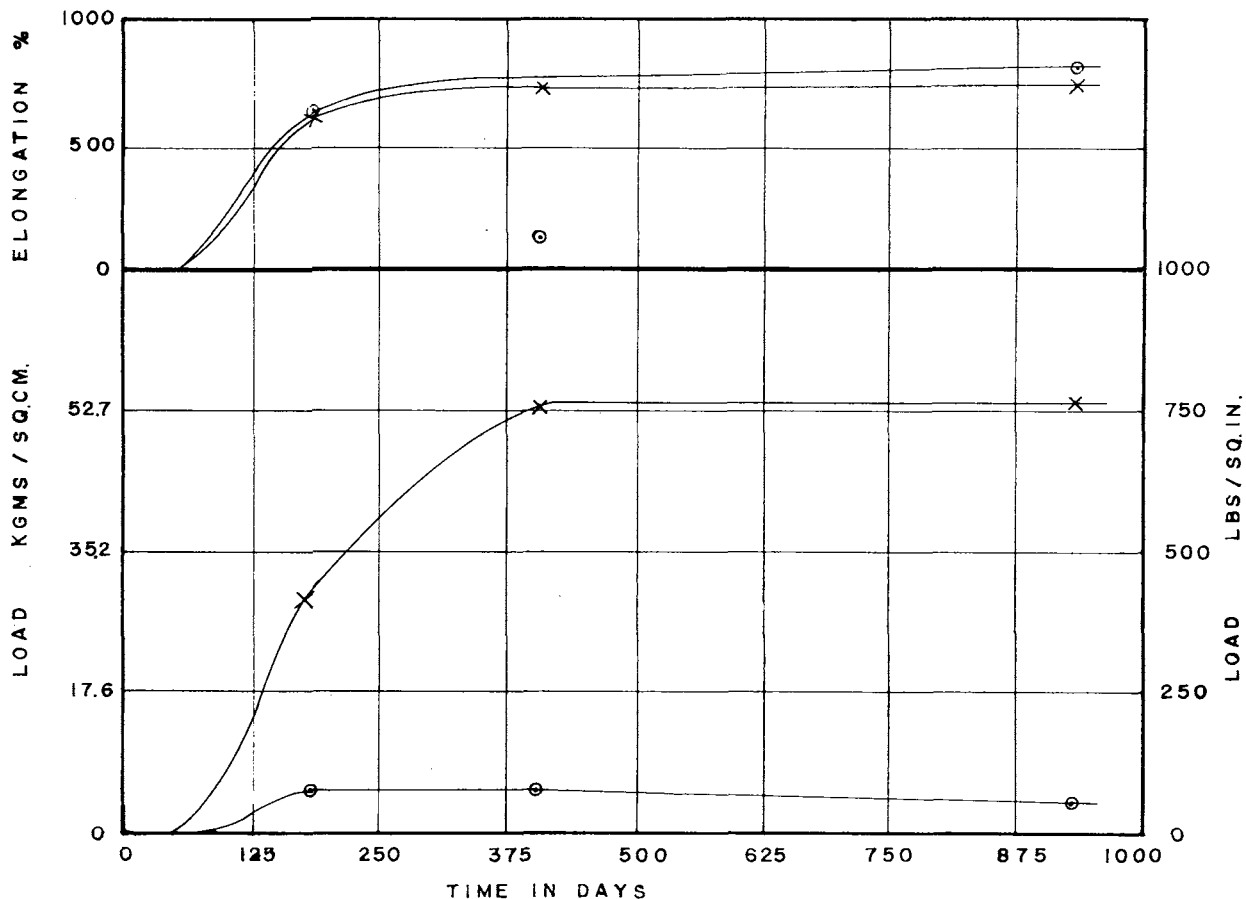


Fig. 3. Plot of vulcanization time vs. (top) elongation and (bottom) tensile strength against grain of vulcanizates obtained: (X) with quinone dioxime; (O) without quinone dioxime.

powdered quinone dioxime at room temperature no signs of vulcanization appeared in over 17 weeks. Similarly, in the same time calendered pale crepe containing 2 parts of quinone dioxime in 100 parts of pale crepe at room temperature gave no signs of vulcanization.

### Experimental

The following recipe was used: pale crepe rubber, 100 parts; yellow mercuric oxide, 10 parts. This was mixed and calendered to 0.062 in. One portion was set aside flat between Holland cloth, and another portion was embedded in quinone dioxime powder in a covered Petri dish. Both were allowed to remain at room temperature and were tested periodically for tensile strength. The test pieces were pulled with the grain. The results are given in Table II.

These results are shown graphically in Figure 3.

This article covers chiefly some work done when the author was with the United States Rubber Company.

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### Synopsis

Calendered sheets of pale crepe rubber containing an ultra-accelerator, piperidinium *N*-pentamethylenedithiocarbamate, and zinc oxide were embedded in powdered sulfur and kept at room temperature. Tensile strengths up to 294.2 kg./cm.<sup>2</sup> (4185 psi) and elongations up to 530% were attained; the combined sulfur in 115 weeks was 3.60%. Calendered pale crepe rubber containing 10 parts of yellow mercuric oxide to 100 parts of rubber allowed to stand covered with quinone dioxime (GMF) powder at room temperature slowly vulcanizes, reaching a tensile strength of 53.1 kg./cm.<sup>2</sup> (754 psi) in 405 days, and retaining this condition for at least twice this same period of time. The elongation reached 740%, and the set was 0.16. The tensile strength obtained is almost as high as that obtained in a press cure with quinone dioxime alone. The untreated sample containing yellow mercuric oxide alone showed a tensile strength of only 5.3 kg./cm.<sup>2</sup> (75 psi). Calendered pale crepe with no mercuric oxide set in quinone dioxime and calendered pale crepe containing 2 parts of quinone dioxime, when allowed to stand at room temperature, showed no signs of vulcanization.

### Résumé

Des feuilles calendrées de caoutchouc crêpe contenant un super-accélérateur, le *N*-pentaméthylènedithiocarbamate de piperidinium, et de l'oxyde de zinc ont été enrobées dans du soufre en poudre et gardées à température de chambre. On a ainsi atteint de forces à la traction de 294,2 Kg/cm<sup>2</sup> et des élongations jusqu'à 530%. Le soufre combiné endéans 115 semaines était de 3,6%. Du caoutchouc crêpe calendré contenant 10 parts d'oxyde jaune de mercure pour 100 parts de

caoutchouc et couvert de poudre de quinone dioxime (GMF), à température de chambre se vulcanise lentement; il atteint une force à la traction de 53,1 Kg/cm<sup>2</sup> en 405 jours et garde encore cette propriété au moins durant une période de temps double. L'élongation atteint 740%; la contraction s'élève à 0.16. La force à la traction obtenue est pratiquement aussi élevée que celle obtenue par un traitement sous pression avec de la quinone-dioxime seule. L'échantillon non-traité et contenant uniquement de l'oxyde jaune de mercure manifestait une force de traction uniquement de 5,3 Kg/cm<sup>2</sup>. Du crêpe calendré sans oxyde de mercurique dans la quinone-dioxime et du crêpe calendré contenant deux parts de quinone-dioxime, ne manifestaient aucun signe de vulcanisations, lorsqu'on les abandonne à température de chambre.

### Zusammenfassung

Am Kalandrer behandelte helle Crepekautschukfelle, die einen Ultra-beschleuniger, Piperidin-*N*-pentamethylenedithiocarbamat, und Zinkoxyd enthalten, wurden in gepulverten Schwefel eingebettet und bei Raumtemperatur gehalten. Zugfestigkeiten bis zu 294,2 kg/cm<sup>2</sup> (4185 lb/in<sup>2</sup>) wurden erhalten; die Dehnungen betragen bis zu 530% und in 115 Wochen wurden 3,60% Schwefel gebunden. Am Kalandrer behandelte heller Crepekautschuk mit einem Gehalt von 10 Teilen gelbem Quecksilber-II-oxyd auf 100 Teile Kautschuk, den man mit Chinondioxim-(GMF)-pulver bedeckt bei Raumtemperatur stehen lässt, vulkanisiert langsam, erreicht nach 405 Tagen eine Zugfestigkeit von 53,1 kg/cm<sup>2</sup> (754 lb/in<sup>2</sup>) und behält diese für mindestens die doppelte Dauer bei. Die Dehnung erreichte 740% und der Set war 0,16. Die Zugfestigkeit ist fast so hoch wie die bei Vulkanisation in der Presse mit Chinondioxim allein erhaltene. Die unbehandelte Probe mit einem Gehalt an gelbem Quecksilber-II-oxyd allein zeigt nur eine Erhöhung der Zugfestigkeit von 5,3 kg/cm<sup>2</sup> (75 lb/in<sup>2</sup>). Am Kalandrer behandelte heller Crepe ohne Quecksilber-II-oxyd in Chinondioxim und am Kalandrer behandelte heller Crepe mit einem Gehalt von 2 Teilen Chinondioxim, jede Partie bei Raumtemperatur gehalten, zeigten keine Zeichen von Vulkanisation.

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