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# The Determination of Zinc Oxide in Rubber Vulcanizates by X-Ray Diffraction*

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## INTRODUCTION

Zinc oxide is a necessary component in most accelerator-sulfur vulcanization systems. While it is not an accelerator, its presence leads to increased modulus, i.e., tighter cures. The manner in which it can effect this better cure is not completely clear. Some insight into the role of zinc oxide has been gained through the analysis of the vulcanizate for reaction products of zinc, such as zinc stearate, the zinc salts of the accelerators, and zinc sulfide. However, these products may not account for all of the zinc oxide which has reacted. An analytical method for the direct determination of unreacted zinc oxide in vulcanizates was therefore needed.

The determination of zinc oxide in rubber vulcanizates has received scant attention. Wet-chemical techniques for analysis of the sample after ashing provide only the total amount of zinc from which the amount of unreacted zinc oxide cannot be determined.

Endter[1] has reported the use of the Debye-Scherrer x-ray technique for the identification of zinc oxide in rubber samples. While similar to the method developed in this laboratory, Endter employed photographic film for recording the diffraction pattern, and special sample preparation was required to accommodate the photographic technique. This method was satisfactory for qualitative identification of zinc oxide, but was difficult to use for quantitative analysis.

Subsequent to this investigation Hagino et al.[2] described the use of x-ray diffractometry for the determination of the mixing ratio of ingredients compounded in rubber. This method was also suggested for the quantitative analysis of zinc oxide, but no studies were reported.

During a study in this laboratory to determine

the role of zinc oxide in the vulcanization of rubber, a new analytical method, based on x-ray diffractometry, was developed. The method was rapid, nondestructive, and simple. The data were reliable and accurate.

## EXPERIMENTAL

### Materials

All materials used to prepare the vulcanized samples were commercially available. Natural rubber was No. 1-ribbed smoked sheet. The reinforcing fillers were of two types: a fine-particle, hydrated, amorphous silica, (Hi-Sil 233, Columbia-Southern Chemical Corp.) and a high-abrasion furnace (HAF) carbon black, (Philblack O, Phillips Chemical Co.). The zinc oxide ($\geqslant 99\%$ purity) was Black Label Type XX72 (New Jersey Zinc Co.). Spider Brand sulfur was used in all compounding. The remaining curing ingredients were rubber-grade products obtained from a variety of sources: MBTS (2,2'-dithiobisbenzothiazole), DOTG (di-o-tolylguanidine), PBNA (phenyl-β-naphthylamine), and TEA (triethanolamine).

### Compounding and Vulcanization

Natural rubber compounds were prepared according to the recipes of Table I. The filler and

TABLE I
Compound Recipes

|  | A, parts by weight | | | | B, parts by weight | | |
|---|---|---|---|---|---|---|---|
| Natural rubber | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Amorphous silica or HAF black | 50 | 50 | 50 | 50 | 0 | 20 | 50 |
| Zinc oxide[a] | 2.5 | 5.0 | 7.5 | 10.0 | 5 | 5 | 5 |
| Curatives[b] | 7 | 7 | 7 | 7 | 7 | 7 | 7 |
| Stearic acid | 0 | 0 | 0 | 0 | 3 | 3 | 3 |

[a] Added as 50% master batch in natural rubber.

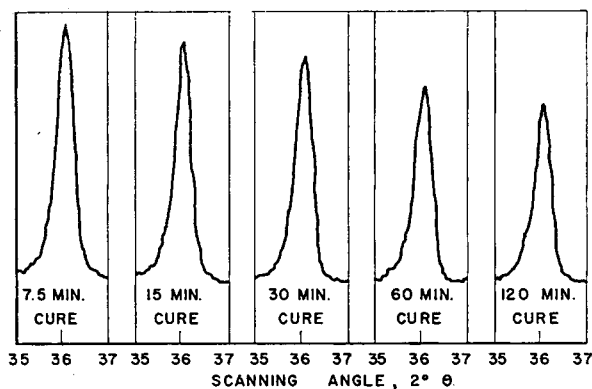[b] Sulfur, 3.0; MBTS, 0.8; DOTG, 1.2; TEA, 1.0; PBNA, 1.0.

Fig. 1. Typical ZnO diffraction patterns from a rubber vul-
canizate.

rubber were mixed in an internal mixer (Banbury-
size B), and the remaining components were added
on a 6 × 12-inch rubber mill. Zinc oxide was
added as a 50% masterbatch in natural rubber.
After sheeting from the mill at 0.075-in. gage,
the compounds were cured between aluminum
foil (0.004 in. thick) in preheated laboratory
presses at 142°C. and 2000 psi. Immediately
after removal from the molds, the cured samples
were cooled in water.

## Diffractometric Analysis for Zinc Oxide

The foil was removed from the cured tensile
sheets, and samples measuring $1^3/_8 \times 1^1/_2$ in. on
a side were cut out. The sample was placed
on top of a standard x-ray sample holder made from
aluminum and then inserted in the goniometer
for scanning. A Norelco geiger counter diffrac-
tometer employing CuKα radiation was used
in the determinations. The conditions throughout
this study were: 35 kv., 15 ma. on a copper target
tube, a nickel filter to remove CuKβ radiation,
a 1° divergent slit, 0.006-in. receiving slit, 1°
scatter slit, and the usual Soller slits to collimate
the beam. The sample was scanned at the rate
of $1/_2°$ per minute from an angle of 37° to 35°
2θ, with a scale factor of 32 and a time constant
of 2 sec. The variation in x-ray intensity was
recorded on a strip chart. A typical diffraction
pattern for a series of cures is shown in Figure 1.

The area of the sample permitted two deter-
minations to be made on each side. From the dif-
fraction pattern, the intensity of the zinc oxide
peak above background, at an angle of 36.2° 2θ
was measured for each determination. The aver-
age of the four measurements was then plotted
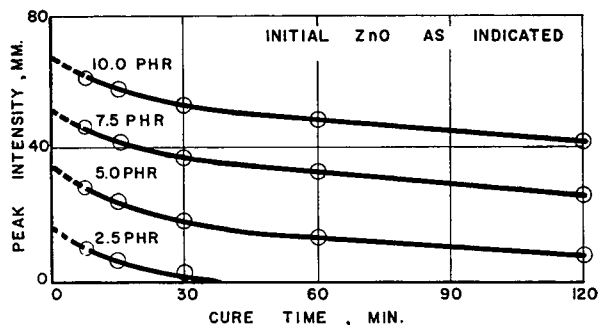against the corresponding time of cure. Smooth



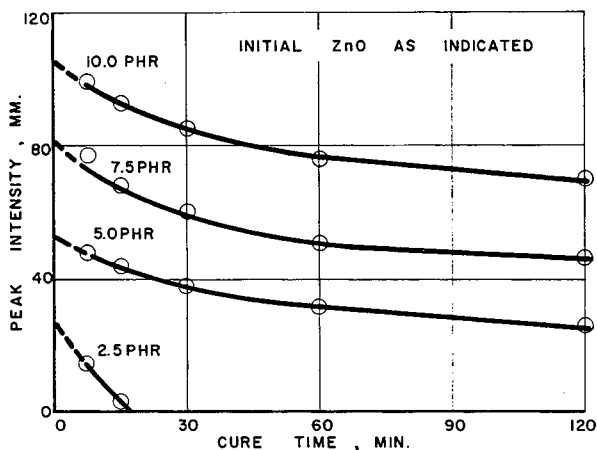Fig. 2. Variation in peak intensity in silica-filled vulcani-
zates.



Fig. 3. Variation in peak intensity in black-filled vulcani-
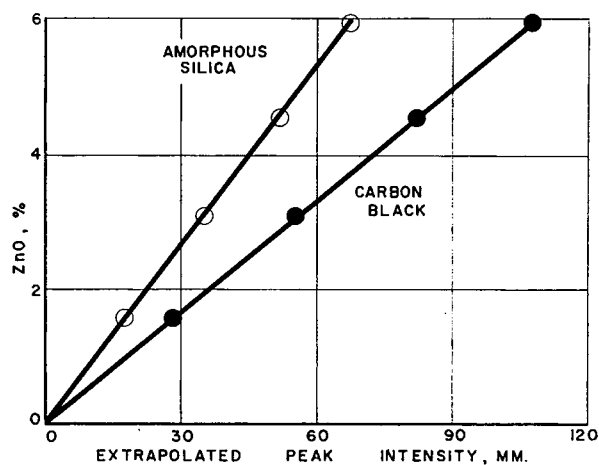zates.



Fig. 4. Variation of peak intensity with ZnO concentration.

curves were drawn through each series of experi-
mental points and extrapolated to zero cure time
(Fig. 2 and 3). The value of the peak intensity
at zero cure time, obtained by extrapolation,
then corresponded to the initial zinc oxide concen-

tration. Calibration curves were obtained by plotting this extrapolated peak intensity against the initial percentage of zinc oxide (Fig. 4).

## DISCUSSION OF RESULTS

In order to obtain the relation between the diffraction intensity and the concentration of zinc oxide, the peak intensity at known concentrations must be determined. If it is assumed that no reaction of zinc oxide occurs prior to curing, the diffraction peak intensity of the uncured rubber compounds can be used. However, attempts to obtain the diffraction pattern before curing resulted in erratic measurements. This was due to the rough surface and the soft nature of the sample, both of which prevented a uniform orientation of the specimen in the goniometer. As a result of this, wide variations of the peak intensity occurred when measuring the four different areas of the uncured sample.

The diffraction peak intensity in the uncured compounds could be estimated with reasonable accuracy by extrapolation of the peak intensity-cure time curve to zero cure time. This was done in Figures 2 and 3 for the compounds of Table IA. Though the peak intensity-cure time curves were nonlinear, smooth curves through the experimentally determined points permitted extrapolation with an estimated relative error of less than ±5%. This error will vary depending on the slope of the curve at zero time of cure. This, in turn, is dependent on the rate of disappearance of the zinc oxide.

The variation of the extrapolated peak intensity with the initial zinc oxide concentration (Fig. 4) was linear, and the curve passed through the intercept of the two coordinates. The silica-filled vulcanizates had correspondingly lower peak intensities than the vulcanizates containing carbon black. This was expected on the basis of the predicted greater absorption of x-radiation by silica than by carbon black.

The differing absorption of x-radiation between silica and carbon black means, of course, that individual calibration curves must be obtained for each vulcanizate which differs in the amount or type of filler. Ordinarily this would require a study of the variation of peak intensity with zinc oxide concentration for each rubber compound which had a different degree of x-ray absorption. Since, however, the plot of peak intensity versus zinc oxide concentration was linear and also passed through the origin, a reasonably accurate calibra-
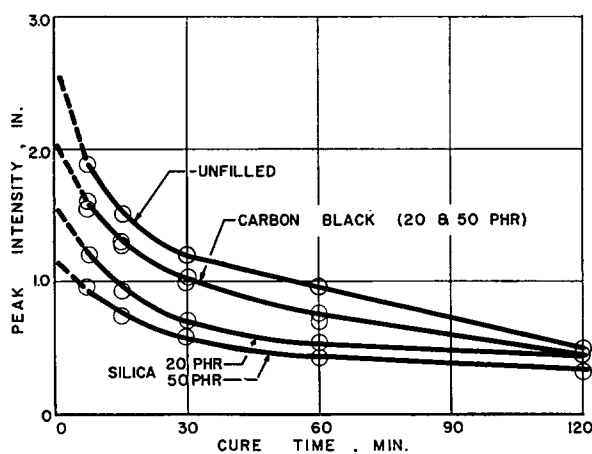


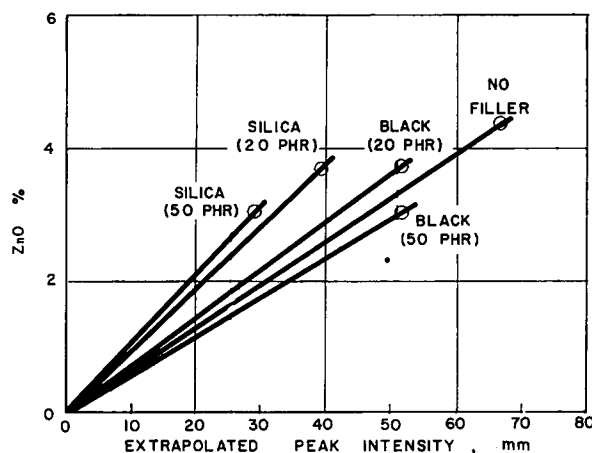Fig. 5. Variation in peak intensity for compounds of table IB.



Fig. 6. Zinc oxide calibration for compounds varying in filler loading.

tion curve can be made from a single value of the extrapolated peak height. This can be obtained for any vulcanizate for which a series of cures is available, provided that short cure times are included in order to follow the initial rapid decrease in the peak intensity.

The peak intensity-cure time curves (Fig. 5) for the compounds of Table IB had a greater rate of change of intensity in the region of the extrapolation than those of Table IA. The presence of stearic acid in the one series of compounds probably accounts for the increased rate of zinc oxide disappearance through the formation of zinc stearate. As a result of this increased rate of change, the extrapolation was somewhat less accurate for the series containing stearic acid.

The single value of extrapolated peak intensity obtained for each vulcanizate from Figure 5 was
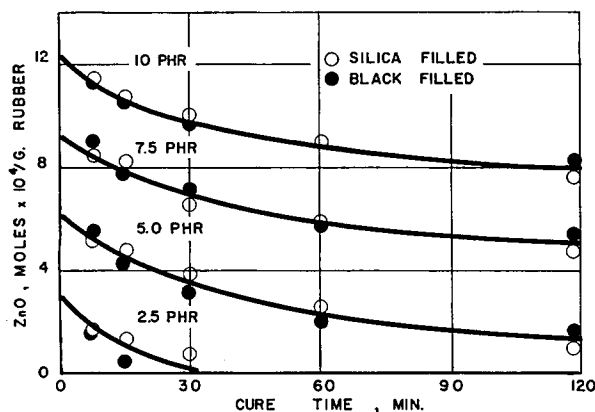
Fig. 7. Rate of ZnO disappearance at various initial ZnO contents.

used for the calibration curves of Figure 6. Again, the curves for the silica-filled vulcanizates had greater slopes than those with carbon black. Because of the relatively low absorption of x-rays by carbon black, the curve for the vulcanizate containing no filler was very similar to those of the black-filled vulcanizates. The differences between these could be attributed to the error of extrapolation or to variations in x-ray scattering caused by different degrees of dispersion of the small particles of carbon black.

By expressing concentrations as moles of zinc oxide per gram of rubber, we eliminated any variations due to differences in compounding ratios. Examination of the rate of change of zinc oxide concentration for each of the vulcanizates on this basis was made for the compounds of Table IA in Figure 7 and those of Table IB in Figure 8. It was at once apparent that the change in zinc
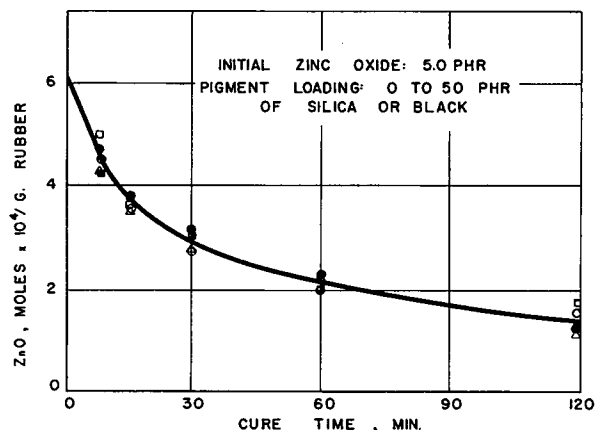
oxide concentration was not dependent on the amount or type of filler.

It is known that zinc oxide is required in this type of curing system in order to obtain a high modulus. This implies that zinc oxide is instrumental in the development of crosslinks, since a high modulus is indicative of a high degree of crosslinking. Yet the addition of reinforcing fillers, which also increased the modulus, had no effect on the rate of disappearance of zinc oxide. The point to be made is that the presence of zinc oxide is necessary for maximum crosslinking, but the consumption of zinc oxide apparently is independent of this crosslinking.

The major cause for the disappearance of zinc oxide can be attributed to the formation of zinc sulfide (Tables II and III). Analysis of the

TABLE II
Formation of ZnS at Various ZnO Concentrations

| Filler, 50 PHR | Initial ZnO, PHR | (Moles ZnS formed/Moles ZnO consumed) × 100 | | |
| --- | --- | --- | --- | --- |
| | | 7.5 min. cure | 30 min. cure | 120 min. cure |
| Silica | 2.5 | 34 | 47 | 71 |
| | 5.0 | 30 | 52 | 51 |
| | 7.5 | 33 | 52 | 56 |
| | 10.0 | 25 | 35 | 59 |
| Black | 2.5 | 92 | 77 | 81 |
| | 5.0 | 100 | 81 | 69 |
| | 7.5 | 100 | 100 | 88 |
| | 10.0 | 100 | 87 | 76 |

TABLE III
Formation of ZnS at Various Filler Loadings

| Filler | (Moles ZnS formed/Moles ZnO consumed) × 100 | | |
| --- | --- | --- | --- |
| | 7.5 min. cure | 30 min. cure | 120 min cure |
| None | 88 | 70 | 75 |
| Silica (20 PHR) | 77 | 67 | 67 |
| Silica (50 PHR) | 24 | 39 | 46 |
| Black (20 PHR) | 82 | 73 | 71 |
| Black (50 PHR) | 65 | 64 | 71 |



Fig. 8. Rate of ZnO disappearance at various filler loadings.

vulcanizates for zinc sulfide, essentially by the method of Adams and Johnson,[3] indicated that zinc sulfide accounted for 65–100% of the reacted zinc oxide in the compounds containing no filler or containing HAF black. On the other hand, only 24–77% of the reacted zinc oxide appeared as zinc sulfide in the presence of amorphous silica. Also, whereas increasing amounts of carbon black

had only a small effect on the amount of zinc oxide converted to zinc sulfide, 50 PHR of amorphous silica caused a large reduction in the formation of zinc sulfide, as shown in Table III. This reduction in zinc sulfide was accompanied by a reduction in the crosslink density (Table IV), as determined by the equilibrium swelling technique of Adams and Johnson.[3] The crosslink density in the presence of carbon black increased (Table IV), but no corresponding change in the formation of zinc sulfide was observed (Table III).

TABLE IV
Crosslink Density as a Function of Filler Loading

| Filler | Crosslink density, moles × 10⁴/g. of rubber | | |
| | 7.5 min. cure | 30 min. cure | 120 min. cure |
| --- | --- | --- | --- |
| None | 1.0 | 1.2 | 1.1 |
| Silica (20 PHR) | 1.0 | 1.2 | 1.1 |
| Silica (50 PHR) | 0.7 | 1.0 | 0.9 |
| Black (20 PHR) | 1.3 | 1.5 | 1.4 |
| Black (50 PHR) | 1.6 | 2.1 | 2.1 |

If the view of Armstrong, Little and Doak[4] that zinc sulfide formation is a measure of mono- and disulfide crosslinks is accepted, then amorphous silica (at 50 PHR) effects a reduction in these types of crosslinks. However, it does so without influencing the rate of reaction of zinc oxide since this was found to be independent of the amount and type of filler (Figs. 7 and 8). Carbon black, on the other hand, apparently introduced additional crosslinks which did not result in the formation of zinc sulfide, since the presence of carbon black had little effect on the amount of zinc sulfide formed. This may indicate that carbon black has introduced crosslinks independent of the sulfur crosslinks, or that it merely influenced the formation of sulfur crosslinks by a mechanism which did not involve the formation of zinc sulfide.

The question concerning the fate of the zinc atoms that were not utilized for the formation of zinc sulfide cannot be resolved, since complete analyses of the vulcanizates were not attempted. There remain several other reactions by which zinc oxide could be consumed. Reaction with the accelerator, MBTS, to form the zinc salt of 2-mercaptobenzothiazole would account for a part of the reacted zinc oxide. Fatty acids which are present in natural rubber or which are added to the rubber compounds would utilize an additional

amount. That this did occur was indicated by the greater initial rate of reaction of zinc oxide (Fig. 8) for the compounds containing added stearic acid than that in the absence of the added acid (Fig 7).

As Brooks, Boggs, and Ewart[5] have shown, amorphous silica is capable of reacting with zinc stearate to liberate stearic acid which then can react with additional zinc oxide. The rubber compounds containing both silica and fatty acids thus may provide yet another means by which zinc oxide is consumed.

Though not substantiated, reaction of zinc oxide with triethanolamine or di-o-tolylguanidine may afford still another route for its disappearance. Zinc salts have been found to form coordinate complexes with nitrogen- and oxygen-containing compounds.[6]

In summarizing, a new technique for the determination of zinc oxide in rubber vulcanizates has been developed which involves the use of x-ray diffractometry. The method is rapid, nondestructive, and has a relative error of less than ±10% of the amount of zinc oxide present. The application of the technique to some typical rubber vulcanizates has demonstrated that the rate of disappearance of zinc oxide is independent of the amount or type of reinforcing filler present. This has led to some interesting observations which may aid in defining the role of zinc oxide in vulcanization.

### References

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2. Y. Hagino, Y. Hirata, T. Yokoyama, and G. Hashizume, *Nippon Gomu Kyôkaishi*, **29**, 1033 (1956).

3. H. E. Adams and B. L. Johnson, *Ind. Eng. Chem.*, **45**, 1539 (1953).

4. R. T. Armstrong, J. R. Little, and K. W. Doak, *Ind. Eng. Chem.*, **36**, 628 (1944).

5. M. C. Brooks, F. W. Boggs, and R. H. Ewart, "The Influence of the Chemical Nature of the Surface of a Filler upon its Reinforcement Properties," paper presented to the German Rubber Society Meeting, Cologne, May 7–10, 1958.

6. N. V. Sidgwick, *The Chemical Elements and their Compounds*, Vol. I, Clarendon Press, Oxford, 1950, pp. 280–84.

## Synopsis

The important role of zinc oxide in accelerated rubber vulcanization has not been thoroughly defined. One major void in the investigations reported has been the absence of a suitable analytical method for following the rate of disappearance of zinc oxide. A method based on x-ray diffractometry is here presented for the direct determination of zinc oxide in rubber vulcanizates. The technique employed is rapid and nondestructive and has a relative error less than ±10% of the amount of zinc oxide present. Application to typical accelerated rubber vulcanizates has shown that the rate of zinc oxide disappearance was independent of the amount and type of reinforcing filler. It was found also to be independent of the degree of crosslinking despite the known dependence of high level crosslink formation on the presence of zinc oxide in this type of curing system. The major part of the reacted zinc oxide appeared as zinc sulfide.

## Résumé

Le rôle important de l'oxyde de zinc dans la vulcanisation rapide du caoutchouc n'a pas été défini entièrement. Un lacune majeure dans les études rapportées étiat l'absence d'une méthode analytique convenable pour suivre la vitesse de disparition de l'oxyde de zinc. On présente ici une méthode basée sur la diffractométrie aux rayons-x en vue d'une détermination directe de l'oxyde de zinc dans les vulcanisates de caoutchouc. La technique utilisée est rapide et nondestructive et comporte une erreur relative inférieure à ±10% de la quantité d'oxyde de zinc présent. L'application à des vulcanisates rapides de caoutchouc typiques à montré que la vitesse de disparition de l'oxyde de zinc était indépendante du degré de pontage malgré la dépendance bien connuee la formation importante de ponts suite à la présence d'oxyde de zinc dans ce type de procédé. La partie principale de l'oxyde de zinc qui a réagi apparait comme sulfure de zinc.

## Zusammenfassung

Die wichtige Rolle des Zinkoxyds bei der beschleunigten Kautschukvulkanisation wurde noch nicht völlig aufgeklärt. Einer der Hauptmängel bei den bisherigen Untersuchungen war das Fehlen einer geeigneten analytischen Methode zur Verfolgung der Geschwindigkeit des Verbrauches des Zinkoxyds. In der vorliegenden Arbeit wird eine Röntgenbeugungsmethode zue direkten Bestimmung von Zinkoxyd in Kautschukvulkanisaten beschrieben. Das verwendete Verhahren ist rasch und zerstörungsfrei und hat einen relativen Fehler kleiner als ±10% der vorhandenen Menge Zinkoxyd. Die Anwendung auf typische beschleunigte Kauschukvulkanisate zeigte, dass die Geschwindigkeit des Zinkoxydverbrauches unabhängig von Menge und Art des Verstärkungsfüllstoffes ist. Ebenso wurde gefunden, dass sie, ungeachtet der bekannten Abhängigkeit der Bildung hochgradiger Vernetzung von der Anwesenheit von Zinkoxyd bei diesem Typus von Vulkanisations-system, unabhängig vom Vernetzungsgrad war. Der Hauptteil des umgesetzten Zinkoxyds trat in Form von Zinksulfid auf.