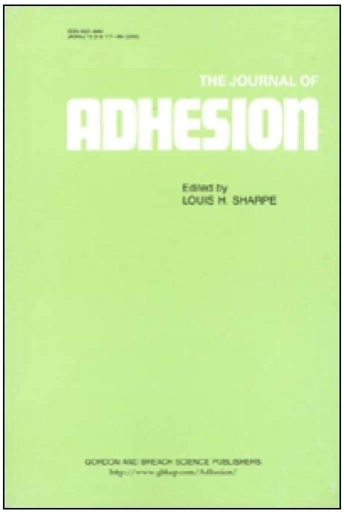

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NOTE

Brass Powder in Rubber Vulcanizates. The Effect on Adhesion

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INTRODUCTION

Brass plating is presently used for promoting the adhesion of rubber to steel cords used in tires. It is generally accepted that the adhesion is due to chemical bonds that are formed between the rubber and brass,[1] although evidence has been obtained indicating that the adhesion is the result of a physical phenomenon.[2] In addition, a catalytic oxidation theory also has been advanced.[1]

Adhesion of rubber to brass-coated steel wire may be measured by a number of methods including the H-test or U-test[3] but preferably by the TCAT (tire cord adhesion test).[4] A study of the chemical reactions that take place between the rubber and brass at or near the surface of the metal is more difficult to achieve. This usually involves an examination of the surface layers of the metal by some kind of bombardment technique such as ESCA (electron spectroscopy for chemical analysis), AES (Auger electron spectroscopy) or SEM (scanning electron microscopy).[2] Considerable work in this area has been reported in the literature.

A study of the reactions that take place in the adhered rubber layer is even more difficult. This is because the amount of rubber directly in contact with the metal is exceedingly small compared to the total mass of rubber present and cannot be removed for testing. Van Ooij[2] used flat brass specimen which were cured to slabs of rubber. After vulcanization, the brass specimens were separated from the rubber under liquid nitrogen and the rubber, as well as the brass surface, subjected to an ESCA interface analysis combined with depth profiling.

Instead of adhering rubber onto the metal, a more convenient way is to add brass, in the form of a finely divided powder, to the rubber. This can be handled by the customary mixing, curing and testing procedures familiar to present rubber technology and should provide useful information concerning the reactions that take place between the rubber and brass.

EXPERIMENTAL

Natural rubber compounds were prepared on a mill according to the following formulation: 100 parts by weight of natural rubber, 5 zinc oxide, 2 stearic acid, 2 sulfur, 0.5 N-t-butyl-2-benzothiazolesulfenamide(Santocure NS®), 1 WingStay L® and variable amounts of metal powders. Sheets 0.5 mm thick were cured at 150°C to 95% optimum cure as determined by the Monsanto Rheometer. The following powders were used:

Brass powder from New Jersey Zinc Co., #1102 (70 Cu, 30 Zn).

Zinc powder from Mallinkrodt Chemical Co.

Stainless steel powder from Ventron Corp., type 434–1 (82 Fe, 17 Cr, 1 Mo).

Copper powder from Glidden Co., #500RL.

The metal powders all passed 325 mesh in size. As the density of brass is approximately 7.5, 400 parts by weight would be 50 parts by volume per 100 parts of rubber.

Equilibrium swelling measurements were made in toluene for 48 hours at 25°C. Q values were calculated where Q is defined as the grams of toluene per gram of rubber hydrocarbon.

$$Q = \frac{\text{Swollen weight} - \text{Dried Weight}}{\text{Original Weight} \times (100/\text{Formula Weight})} \tag{1}$$

The degree of crosslinking would then be $1/Q$. Crosslinking was also determined from the well-known Flory–Rehner equation[5,6] using a value of 0.43 for the interaction constant.

$$\nu = -\frac{v_r + \chi v_r^2 + \ln(1 - v_r)}{V_s(v_r^{1/3} - v_r/2)} \tag{2}$$

where ν is the number of elastically effective network chains per unit volume of rubber, v_r is the volume fraction of rubber in the swollen vulcanizate, V_s is the molar volume of toluene, and χ the interaction constant between the rubber and toluene.

Cure properties were determined by the Monsanto Rheometer. Stress-strain properties were determined from 0.5 mm thick sheets by an Instron tester. Oxygen absorption measurements[7] were made at 80°C on 0.5 mm cured sheets.

RESULTS AND DISCUSSION

The most generally accepted theory of adhesion holds that there is some kind of bond formed between the rubber in the vulcanizate and copper at the surface of the brass.[1] ESCA measurements indicate that adhesion is the result of a bonding between the rubber and a very thin layer or interfacial film of cuprous sulfide on the brass surface.[2] Equilibrium swelling is a technique in which brass powder, if bonded to the rubber, should restrict the swelling of the vulcanizate immediately surrounding the brass particles and as such could possibly be used as a means for determining the degree of adhesion.[8] Moreover, it would be independent of the time dependent nature of viscoelastic materials such as rubber. This time dependency often obscures the validity of many physical tests including adhesion testing. Apparent crosslinking as determined from swelling data of vulcanizates loaded with brass powder is shown in Figure 1. Zinc and stainless steel powders were included as controls.

Results show that the apparent crosslinking increased with increased loading of brass powder indicating a restriction of the swelling of the rubber

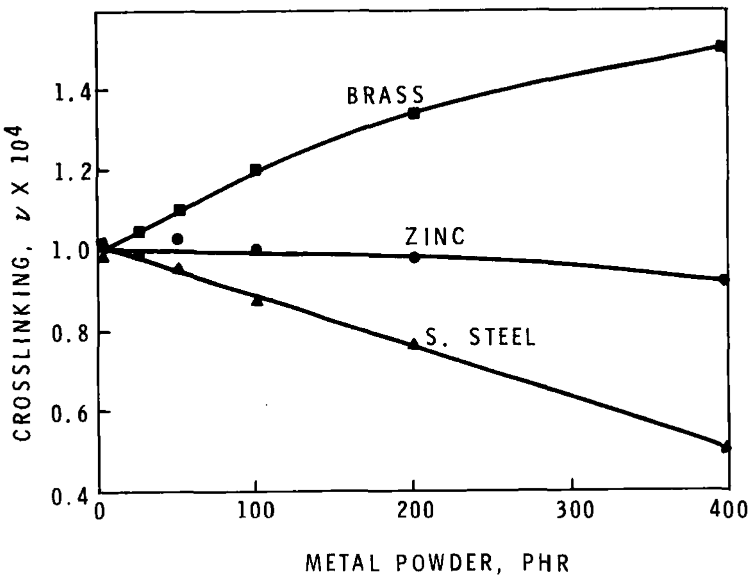

FIGURE 1 Effect of metal powders on crosslinking of natural rubber vulcanizates.

by some kind of interaction. Zinc and especially stainless steel loaded vulcanizates resulted in a decreased crosslinking. Similar results were found using $1/Q$ values which are comparatively simple to calculate compared to the cumbersome Flory–Rehner equation. Results are in agreement qualitatively with the data of van Ooij[2] who found that the adhesion of rubber to brass was 700–1200 N/64 mm^2, rubber to zinc was 100–200 and rubber to steel was zero, using a lap-shear test on an Instron tester.

The interaction between rubber and a filler such as carbon black has been investigated by a number of workers using a swelling technique. Assuming the swelling to be completely restricted at the rubber-filler interface, due to adhesion, Kraus[9] has shown that the degree of restriction on the volume concentration of a reinforcing filler follows an equation of the form

$$\frac{v_{ro}}{v_{rf}} = 1-[3c(1-v_{ro}^{1/3})+v_{ro}-1]\frac{\phi}{1-\phi} \qquad (3)$$

where v_{ro} represents the volume fraction of rubber in the unfilled vulcanizate, v_{rf} is the volume fraction of rubber in the filled vulcanizate, ϕ is the volume of the degree of adhesion. Figure 2 shows this type of plot which predicts that v_{ro}/v_{rf} should vary linearly with $\phi(1-\phi)$. At high concentrations of brass powder, the line deviated from linearity. The theory assumes that the filler particles are far enough apart so as not to interact with each other. This is obviously not true at high loadings. Lack of adhesion of a filler to rubber is apparent by swelling in excess of that predicted by Eq. 3 and indicated by a positive slope in Figure 2. Curves that are not linear indicates that Eq. 3 is no longer obeyed and is exemplified by a whiting- or silica-filled vulcanizate.[10] Effects of different fillers may then be determined by the deviation they produce. According to this criterion, brass showed adhesion to the rubber whereas zinc and stainless steel did not.

Lorenz and Parks[11] also investigated the restriction of swelling by a filler using carbon black in a natural rubber vulcanizate. Their results followed an empirical relation that is exponential in nature:

$$\frac{Q_{\text{Black}}}{Q_{\text{Gum}}} = ae^{-z}+b \qquad (4)$$

where Q_{Black} and Q_{Gum} is the weight of swelling agent imbibed per unit weight of rubber, z is the weight of filler per unit weight of rubber and a and b are constants. This dependence was explained as due to a restricted swelling of the rubber matrix in the neighborhood of filler particles. Porter[12] and also Cunneen and Russell[13] have used v_r instead of Q values to obtain a volume relationship. Data are plotted in Figure 3 where z is defined as the weight of filler per unit weight of total rubber vulcanizate. The constants a and b are

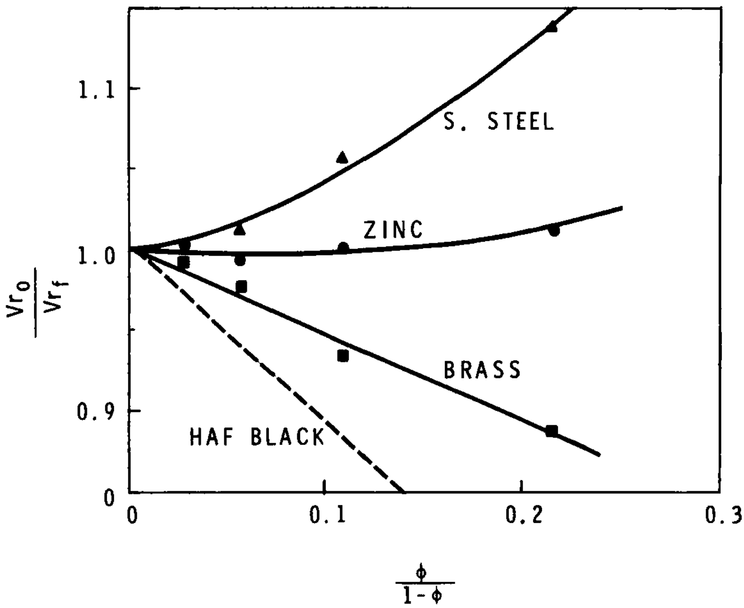

FIGURE 2 Kraus plots of swelling data. Effect of metal powders.

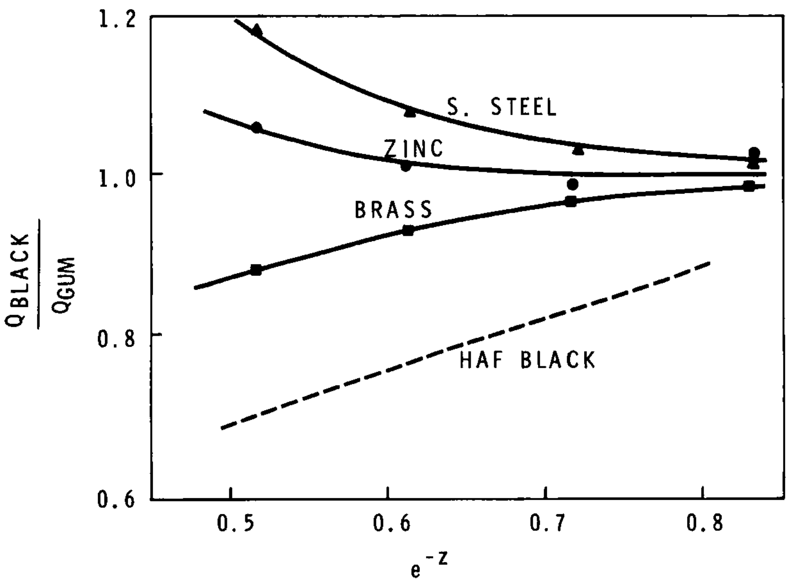

FIGURE 3 Lorenz plots of swelling data. Effect of metal powders.

indicative of relative rubber-filler interaction, high values of a (slope) and low values of *b* (intercept) indicating a strong rubber-filler attachment. Here again, the rubber showed adhesion to brass as compared to zinc and stainless steel.

The exponential relationship in Eq. 4 was found by Porter to be equivalent to a simple relationship between the apparent and actual cross-link concentrations[12]:

$$\frac{N_{\text{apparent}}}{N_{\text{actual}}} = 1 + K\phi \qquad (5)$$

where N_{apparent} is the crosslink density from the Flory–Rehner equation for a filled vulcanizate making allowance for the volume of filler. N_{actual} is the crosslink density for an analogous gum stock. ϕ is the volume fraction of filler in the vulcanizate and K is a constant characteristic of the filler. This relation was used to determine the actual crosslink concentration in filled rubber vulcanizates. Data are plotted in Figure 4 and again show an adhesion of the rubber to brass.

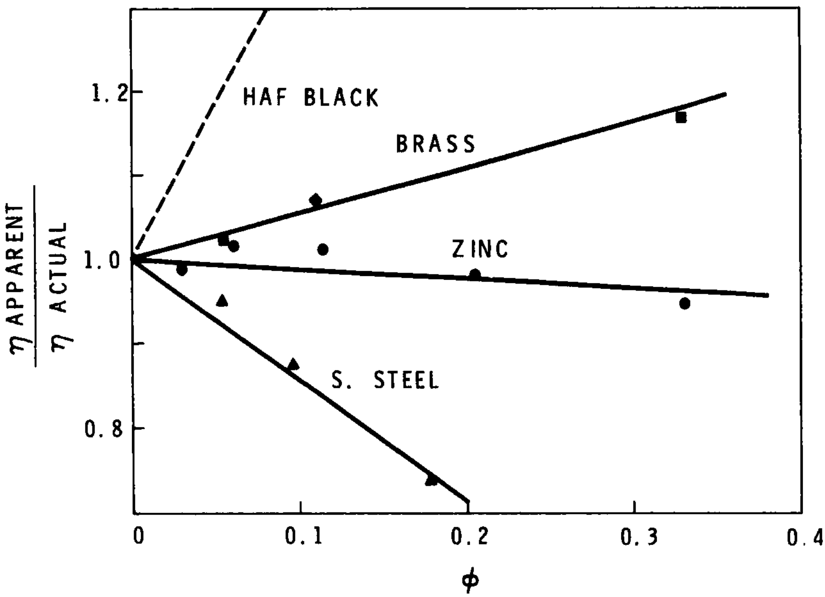

FIGURE 4 Porter plots of swelling data. Effect of metal powders.

Cure Properties

Rheometer data of brass loaded NR stocks are shown in Figure 5. The cure behaviour of zinc and stainless steel loaded stocks were similar to that of brass. This is shown by Westlinning and Wolff's treatment of the Rheometer data where the rubber-filler interaction is described in terms of α_F values.[14]

$$\alpha_F = [(\Delta L_f/\Delta L_g) - 1]/W \tag{6}$$

L_f and L_g stand for the torque measured with filled stock and gum stock, respectively, and W represents the weight of filler, Figure 6. The effect of increased brass, zinc and stainless steel loadings was to increase the maximum torque while decreasing the scorch time and optimum cure time. Data for stocks containing brass powder are shown in Figure 7. The data indicate that the metal is acting to promote or accelerate the crosslinking of the rubber, the effect being quite pronounced.

Whereas brass, zinc and stainless steel powders accelerated the cure, copper powder prevented a cure completely at concentrations of 10 phr or greater, Figure 8. A concentration of 10 phr by weight would be a little over 1 phr by volume and, therefore, represents a small amount. This observation was different from that encountered with brass and was entirely unexpected. It is assumed that the copper reacted with sulfur in the rubber stock forming an insoluble copper sulfide which removed the sulfur from availability as a vulcanizing agent. In brass, the supply of copper is restricted

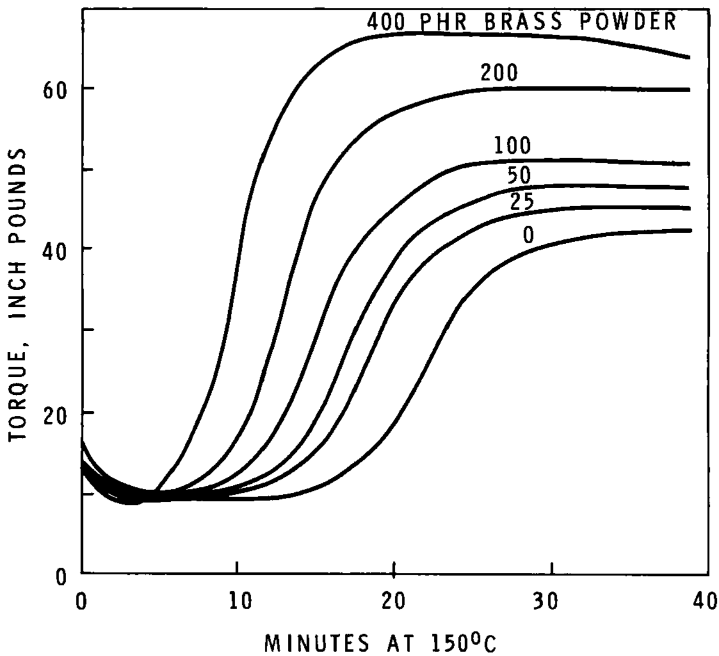

FIGURE 5 Rheometer curves of natural rubber stocks containing brass powder.

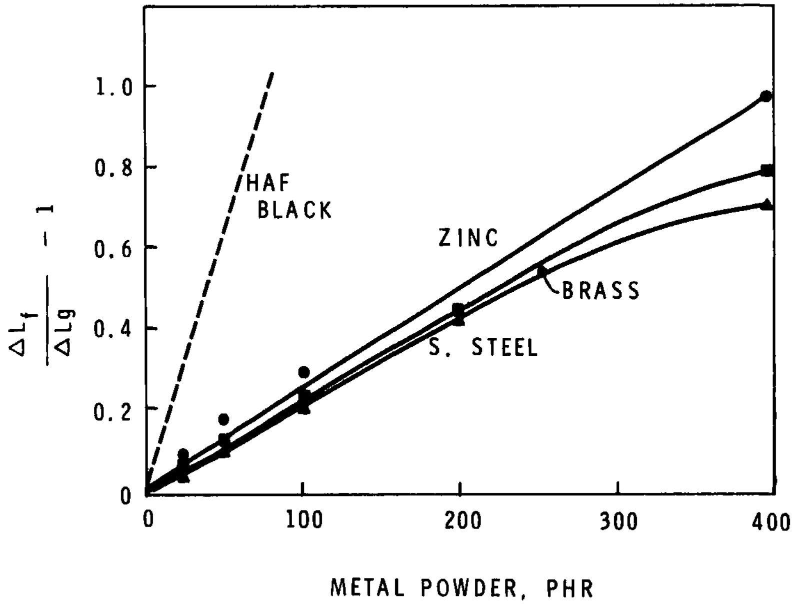

FIGURE 6 Westlinning plots of Rheometer data. Effect of metal powders.

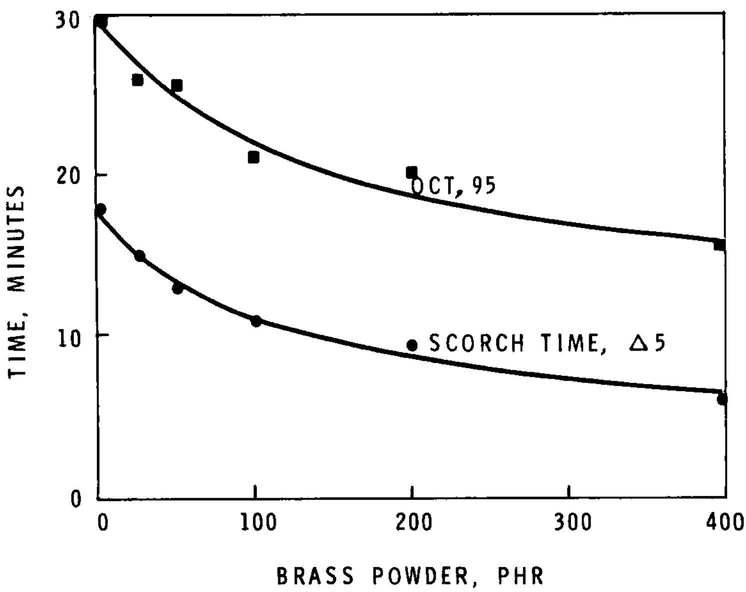

FIGURE 7 Effect of brass powder on scorch time (Δ5) and optimum cure time (95).

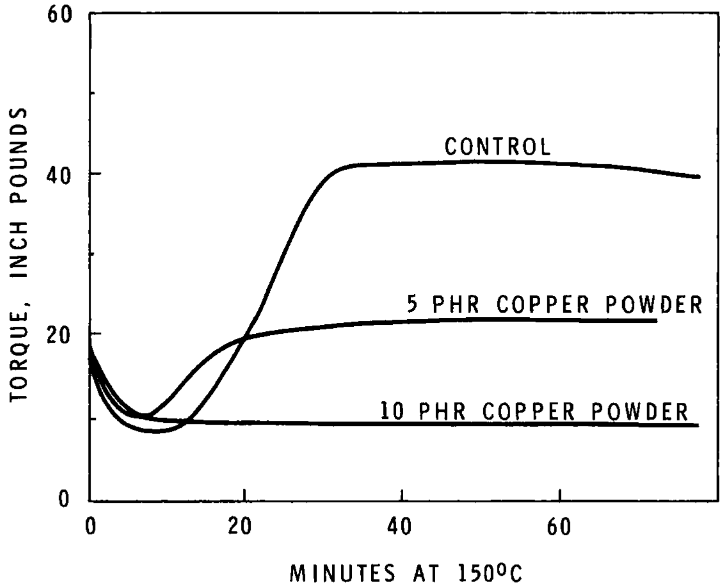

FIGURE 8 Rheometer curves of natural rubber stocks containing copper powder.

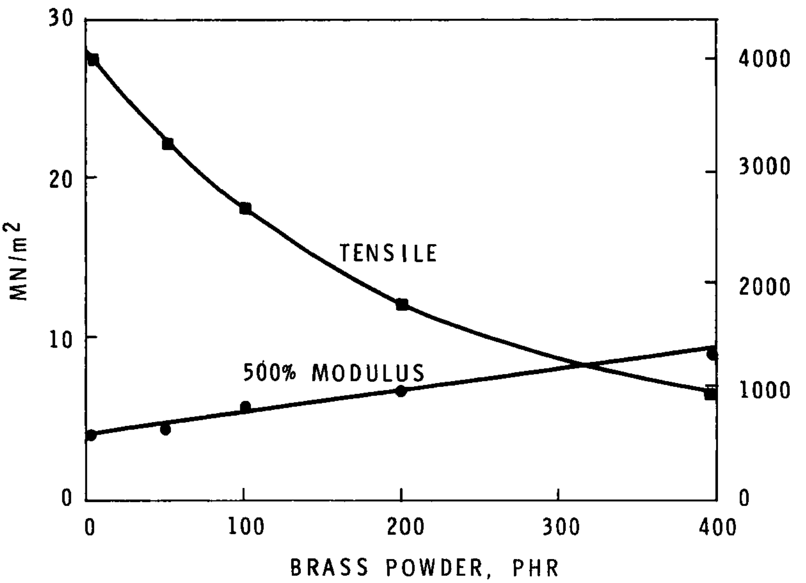

FIGURE 9 Effect of brass powder on stress-strain properties.

by an immediate zinc oxide enriched layer,[2] so that the reactivity of copper is reduced.

The addition of brass, zinc and stainless steel powders resulted in a deterioration of the tensile strength. Studebaker[15] has shown that inhomogeneities such as grit, even in small amounts, markedly reduce the breaking elongation and tensile strength of the rubber. Data for brass loaded vulcanizates are shown in Figure 9.

Modulus values increased slightly with loading thus correlating with swelling measurements. Addition of zinc and stainless steel powders resulted in a small decrease in modulus.

Aging Properties

Brass powder, even in very small amounts, caused an increase in the oxidation of the rubber as evaluated by oxygen absorption measurements, Figure 10. The effect on the rate of oxidation is shown in Figure 11. $1/T$ is taken as the average rate to 1 % oxygen, where T is the time required to absorb 1 % oxygen at 80°C. One of the theories of adhesion suggests that bond formation occurs due to oxidation of the rubber surface at the rubber-brass interface, the copper present in the brass deposit acting as a catalyst of oxidation.[1] It is believed that in order for copper to be effective as an oxidation catalyst, it must be in an ionic form as Cu^{+} or Cu^{++}.[16] The effect of the metal ion on

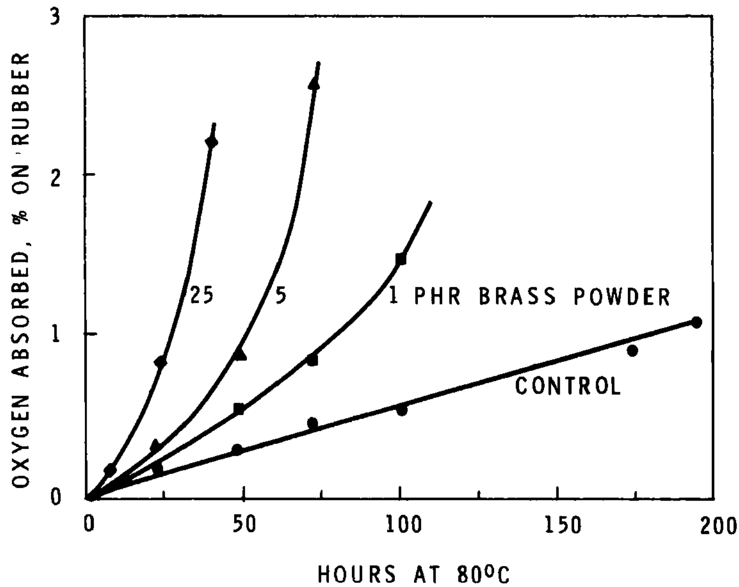

FIGURE 10 Effect of brass powder on oxygen absorption.

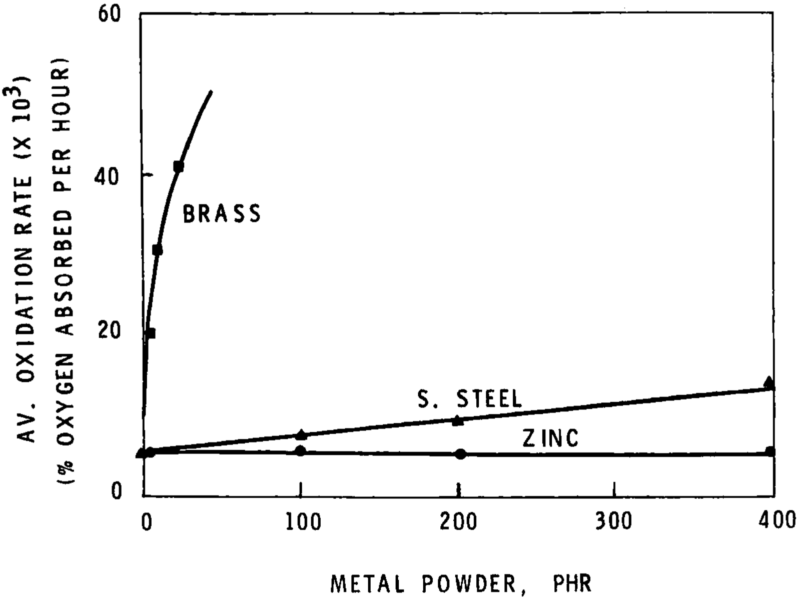

FIGURE 11 Effect of metal powders on rate of oxidation.

on oxidation is to speed up the rate of initiation by accelerating the rate of peroxide decomposition to free radicals.[17]

$$2\,\mathrm{ROOH} \xrightarrow{Cu^{+}/Cu^{++}} \mathrm{RO\cdot} + \mathrm{ROO\cdot} + H_2O \qquad (7)$$

Presented here is a somewhat unique or novel approach to the study of rubber adhesion. The method of adding powdered brass or other material to the rubber should be a useful technique for assessing the degree of adhesion. It should be pointed out, however, that reinforcement of the rubber by brass as determined by crosslink density from swelling measurements is not necessarily proof of adhesion. The observed phenomenon could be due to adhesion between the rubber and brass and/or simply a promotion of the crosslinking by the brass. Additional tests need to be made. Further insight into the mechanism of rubber adhesion may be gained by an extension of the swelling method to different rubbers and to a variation of the curing system.

SUMMARY

Natural rubber vulcanizates loaded with brass powder showed an increase in crosslinking (by swelling measurements), indicating an interaction or bonding between the rubber and brass. Techniques previously employed with reinforcing fillers such as carbon black were used to evaluate the effect

of brass on adhesion. The addition of brass powder decreased the scorch time and optimum cure time indicating that the rubber immediately surrounding the brass was being cured at a faster rate. Copper powder, on the other hand, inhibited the cure completely. When exposed to air or oxygen, even small amounts of brass catalyzed oxidation of the rubber.

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