

Antioxidant Effects during Blade Abrasion of Natural Rubber*

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Synopsis

A blade abrasion device similar to that developed by Champ, Southern, and Thomas has been used to determine the wear rates of several simple carbon black-filled natural rubber materials over a range of frictional loading at room temperature in air. The materials show two mechanisms of wear depending on the amount of frictional load applied. Smearing, the mechanochemical decomposition of the wearing surface leading to a tarlike wear product, occurs at low frictional loads and is replaced by particulate debris created by cohesive rupture at higher frictional loading. It was found that a representative alkyl/aryl paraphenylenediamine and hindered phenol antioxidant were only effective in reducing the rate of wear during smearing, when degradation processes are important. Furthermore, the reduction in wear rate during smearing was quite similar for these two antioxidants.

INTRODUCTION

Abrasion of filled natural rubber (NR) using a blade abrasion device¹ has been shown² to involve a balance between two competing wear mechanisms: mechanochemical breakdown of the rubber surface leading to low molecular weight products (smearing) and fracture on a larger scale leading to particulate debris. The particular NR material used then was quite susceptible to mechanochemical chain scission, smearing in air over the whole range of frictional work inputs examined. Blade abrasion experiments reported here involving a harder NR material, crosslinked with a different sulfur system, show that in this material either wear mechanism can be dominant in air depending on the applied frictional force. This system was a convenient one, therefore, with which to reopen the old question of antioxidant action during abrasion. Answers to date have been contradictory; for instance, Schallamach^{3,4} reports that antioxidants reduce the rate of wear of NR when smearing occurs in air, but have no effect on wear rates when smearing is prevented in an inert atmosphere. In contrast, Brodskii et al.⁵ noted beneficial antioxidant effects in both air and inert gas, while Il'ina et al.⁶ saw no dependence of wear rate on the presence of the same antioxidants during either smearing or particulate wear. One possible reason for these confusing results could be the variability of the wear conditions themselves due perhaps to changes in the coefficient of friction and roughness of the abrasives as the mechanisms of wear changed in the experiments.

The blade abrader can lessen these experimental problems by controlling the frictional work during abrasion and allowing frequent replacement of the razor blade abrasive.¹ In this paper, the blade abrader is used to establish the effect

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of two representative antioxidants on the wear of filled NR under carefully controlled conditions.

EXPERIMENTAL

The blade abrader device and experimental method used in this work is similar to that already reported in the literature.¹ Rubber wheels, about 62.0 mm in external diameter and 13.0 mm wide, were abraded by rotation against a stationary razor blade (Schick® Plus Platinum). During abrasion, the tangential or frictional force F was maintained approximately constant at each value of F which ranged from about 60 to 2000 N/m wheel width. At the speed of rotation of 10 rev/min, no frictional heating of the rubber surface was detectable when the surface was probed with a thermocouple immediately after abrasion. All measurements were made in air at room temperature, $23^{\circ}\text{C} \pm 3^{\circ}\text{C}$. The weight loss by abrasion was measured after steady-state wear conditions were reached and converted into the rate of wear, A , expressed as the change in radial thickness per revolution of the wheel, using the known density of the materials and the surface area of the wheels. As before,^{1,2} the rubber wheels were cleaned during abrasion with sticky tape (Scotch® Magic Transparent # 105) to prevent buildup of debris during the experiment. This was augmented, when smearing occurred, by more prolonged tape cleaning just prior to weighing.

Three simple carbon-black-filled NR materials were abraded in this way. The rubber formulations were all based on SMR5L Natural Rubber and contained 50 phr (parts per hundred rubber) of N220 carbon black. Their formulations are given in the Appendix. The materials differed primarily in the antioxidant systems used in each. Material A contained 2% by weight of rubber of Wingstay® 300 (*N*-1,3-dimethylbutyl-*N'*-phenyl-*p*-phenylenediamine) plus 1% by weight of rubber of wax. In Material B, an equal weight of Antioxidant 2246 (2,2'-methylene-bis(4-methyl-6-*tert*-butyl-phenol), which is within 10% of an equal molar amount replaced the Wingstay® 300, the amount and type of wax remained the same. Material C, the control, contained no added antioxidant or wax. Material A was formulated using a slightly larger amount of curatives in order to obtain mechanical properties which were close to the other two materials. This compensated for the retarding effect of the *p*-phenylenediamine antioxidant on the crosslinking process. The small strain Young's modulus and resilience of the materials before abrasion were measured at room temperature using an indentation technique.⁷ These data were taken after the third indentation cycle, to allow stress softening effects to stabilize.

RESULTS AND DISCUSSION

The three materials had similar small strain Young's modulus E and resilience R (Table I). Their measured wear rates A are shown as a function of the frictional force F in Table II and Figure 1, where a sudden jump in wear rate can be seen in all the materials starting at about 200 N/m frictional load. This is caused by a change in the mechanism of wear: smearing is dominant at low frictional loads but begins to be superseded by particulate debris at a critical force. In the transition region, 200–600 N/m frictional load, where the mechanism of wear is changing, the debris particles are still somewhat tacky and agglomerate into

TABLE I
Small Strain Mechanical Properties at Room Temperature after Stress Softening

	Material A	Material B	Material C
Young's Modulus E (MPa)	5.7	5.2	5.5
Resilience R	0.83	0.70	0.80

cylindrical rolls, sometimes 1 mm in length. The transition probably corresponds to the point at which the rate of rubber removal exceeds the rate of its structural decomposition.

As can be seen from Figure 1, material C wears about three times as quickly as materials A and B during smearing at low frictional loads, but the wear rate of all three materials is indistinguishable at higher loads where particulate debris is forming. Thus, the antioxidants are only effective in reducing the rate of wear of NR during smearing abrasion, when mechanochemically initiated oxidation is the dominant wear process. They have no noticeable effect when physical, cohesive fracture processes are important.

The two antioxidants provide an equal reduction in wear rate during smearing. This could mean that the bulk of structural breakdown during smearing involves oxidative chain scission reactions following mechanochemical initiation because Antioxidant 2246 is known to be an ineffective free radical trap but powerful deactivator of peroxy radicals.⁸

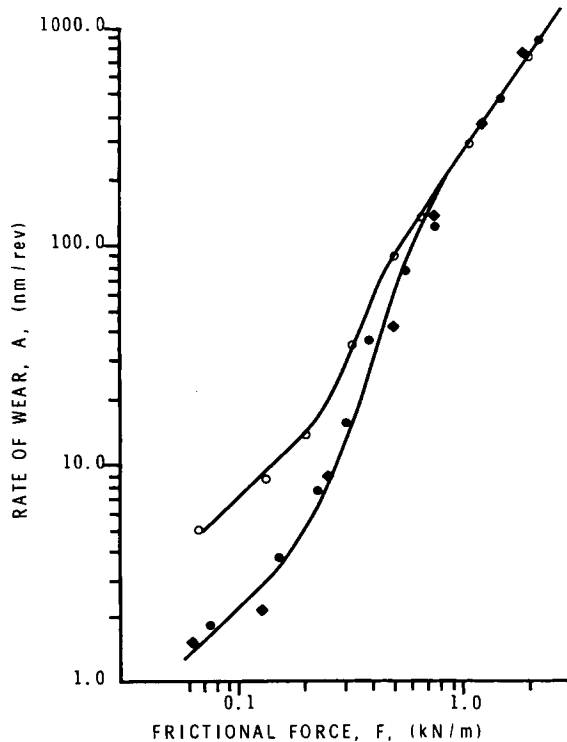


Fig. 1. Wear rate A vs. frictional force F at room temperature: (●) material A; (◆) material B; (○) material C.

TABLE II
Rates of Wear, A , as a Function of Frictional Force F at Room Temperature

Material A			Material B			Material C		
F (N/m)	A (nm/rev)	CV ^a (%)	F (N/m)	A (nm/rev)	CV (T)	F (N/m)	A (nm/rev)	CV (%)
77	1.8	22	64	1.5	13	68	5.0	14
154	3.7	18	129	2.2	11	135	8.7	15
231	7.7	8	257	8.9	11	207	13.6	5
308	15.5	15	514	43.1	20	337	35.0	5
386	37.2	16	771	138.0	2	507	89.5	5
578	77.0	5	1286	367.0	6	676	136.0	5
1543	473.0	7	1929	752.0	4	1014	293.0	1
2315	895.0	2				2027	723.0	1

^a Coefficient of variation of the wear rate data: standard deviation as a percentage of the mean.

CONCLUSIONS

Simple blade abrasion experiments using model-filled natural rubber materials in air at room temperature have shown that wear can occur by one of two completely different mechanisms depending on the level of frictional loading: structural decomposition leading to sticky, tarry debris at low frictional loads and the removal of particulate debris by a fracture process at higher forces. In accord with this observation, antioxidants are effective in reducing the rate of wear of natural rubber only during smearing where degradation is important. The magnitude of the antioxidant effect was not sensitive to the type of antioxidant, at least for the typical alkyl/aryl paraphenylenediamine and hindered phenol additives used here.

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APPENDIX

The rubber formulations in parts by weight, and the vulcanization conditions are given below.

	<u>A</u>	<u>B</u>	<u>C</u>
SMR5L (natural rubber)	100	100	100
ISAF, N220 carbon black	50	50	50
Zinc oxide	3.0	3.0	3.0
Stearic acid	2.0	2.0	2.0
Wingstay 300	2.0	—	—
Antioxidant 2246	—	2.0	—
Paraffin wax	0.5	0.5	—
Microcrystalline wax	0.5	0.5	—
Sulfur	3.25	2.5	2.5
<i>N</i> -cyclohexylbenzothiazyl sulfenamide	1.4	0.8	0.8
Vulcanization time (min) at 150°C	30	45	30

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