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Wear of metal by rubber

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Rates of wear have been determined for steel and bronze scrapers sliding over rubber surfaces. The wear rates were found to depend strongly upon the particular elastomer used, varying by orders of magnitude even though the other ingredients in the compound and the physical properties of the rubber were largely unchanged. In the absence of oxygen the metal scrapers were found to wear away much faster in general; by a factor of 5 to 50 times, depending upon the elastomer. Butyl rubber was anomalous in this respect, however, causing three times greater wear in air than in nitrogen. These diverse observations are attributed to the direct attack upon metals of free radical species generated by mechanical rupture of elastomer molecules during abrasion. The rate of metal wear is closely correlated with the stability of polymeric radicals formed in this way. When the radical is highly reactive it is thought to take part primarily in internal reactions and thus cause little wear of the scraper. On the other hand, relatively stable polymer radicals appear to attack metals vigorously.

1. Introduction

Soft materials are generally worn away when they slide against harder ones. Thus, when rubber testpieces are abraded by sliding past a sharp metal edge, wear of the scraper itself is usually ignored. Nevertheless, the scraper does become worn, and its rate of wear depends in an unexpected way upon properties of the rubber and upon the presence or absence of oxygen in the surrounding atmosphere. This phenomenon has now been examined for a wide range of elastomers, with diverse physical and chemical properties, and for both steel and bronze scrapers. The results are presented below, and discussed in terms of chemical reactions between metals and polymeric free radicals generated during frictional sliding.

Some preliminary observations were reported earlier for a steel scraper worn by two tyre tread elastomer compounds having similar physical, but different chemical, properties [1]. The abrader, a stainless steel razor blade, was found to wear away much more rapidly against a *cis*-polyisoprene (natural rubber) surface than against a *cis*-polybutadiene surface, and much more rapidly in an inert atmosphere than in air. These observations led to the hypothesis, explored further below, that free radical species formed by mechanical rupture of elastomer molecules under sliding conditions can react directly with steel. Related phenomena have been described in studies of metal grinding processes in the presence of polymers, and attributed to the same general mechanism [2–6]. However, in this earlier work, the wear conditions were less well defined and the polymers used were of such varied chemical structure and physical state that direct comparison with the present results does not seem feasible.

2. Experimental

Three metal scrapers were employed in the experiments: a stainless steel razor blade ("Schick Plus Platinum", Schick Safety Razor Company), a knife blade made of unalloyed steel, ASTM C1045, heat-treated and quenched but not tempered, and a knife blade made from an extruded aluminium–bronze copper-base alloy ("Ampco 21", Ampco Metal Company). Measurements were made of the hardness of each blade: they were found to have Rockwell C hardness numbers of over 60, 58 ± 2, and 33 ± 2, respectively.

In the wear experiments, the blade was held at right angles to the outer surface of a cylindrical rubber wheel and pressed against it as shown in

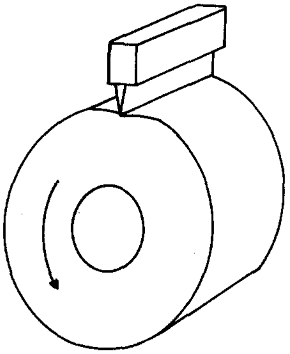

Figure 1 Experimental arrangement for studying abrasive wear of a metal blade, held at right angles to the surface of a solid rubber wheel [7, 8].

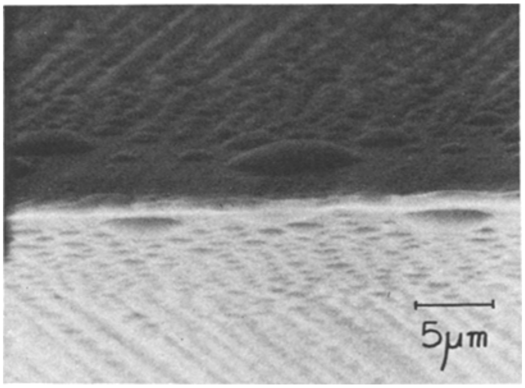

Figure 2 Edge of a new "Schick Plus Platinum" razor blade.

Fig. 1. The wheel rotated at 10 rev min^{-1} about a fixed axis and friction between the blade and the surface of the rubber wheel led to wear of both. This arrangement for studying abrasive wear of rubber is based on that described by Thomas and co-workers [7, 8]. In the present experiments the metal blade was pressed radially against the wheel surface until a frictional force was generated of 1.6 N mm^{-1} of length of blade edge in contact with the wheel surface. The corresponding normal force varied between 0.6 and 1.0 N mm^{-1}, depending upon the coefficient of friction of the rubber wheel (ranging from about 1.6 to 2.7). Both the normal and frictional forces were monitored continuously by means of strain gauges attached to the stiff cantilevered blade holder. At intervals, minor adjustments were made in the position of the blade, by means of a micrometer screw, in order to maintain the frictional force constant.

Wear of the metal blade was determined after 2500 revolutions of the wheel, i.e. after sliding about 500 m over the wheel surface. Measurements were made of the blade tip width, w, using a scanning electron microscope, and of the distance, d, that the blade edge had receded. The volume, v, of metal worn away was then calculated assuming that the blade tip was originally triangular in cross-section. Values obtained in this way were found to be reasonably reproducible, within about ±30%. Relatively large changes in wear rate were observed with different elastomers, as discussed later.

A new "Schick Plus Platinum" razor blade is shown edge-on in Fig. 2. The width of the blade tip initially is seen to be only about 0.5 μm or less. A new blade was also found to be coated with droplets, clearly visible in Fig. 2. These are believed to be a lubricant, possibly Teflon. They were worn off rapidly, within the first 20 m of sliding, and are thought not to affect the experimental results reported here.

The rubber wheels were 25 mm wide, 64 mm o.d. and 25 mm i.d. Their composition is given in the Appendix. All of the wheels contained carbon black and resembled tyre tread rubber. Indeed, in several cases (NR, BR and TPR) the same mix formulation was employed, only the elastomer being changed.

3. Experimental results and discussion

3.1. General observations

Wear of metals has been generally considered to be governed by the magnitude of the frictional force and the relative hardness of the sliding materials. Therefore, it is surprising to find that the wear rate of steel against rubber can vary by a factor of 50 or so (Table I), when both the

TABLE I Wear rate of steel razor blades

Elastomer	Hardness (Shore A)	Test atmosphere	Wear rate × 10^{16} (m^3 rev^{-1})
SBR	75	N_2	100
SMR	60	N_2	40
IIR	57	Air	17
SBR	75	Air	13
IIR	57	N_2	5.2
TPR	67	N_2	5.2
BR	66	N_2	2.5
EPR	56	N_2	1.3
SMR	60	Air	0.75
TPR	67	Air	0.70
BR	66	Air	0.30
EPR	56	Air	0.25

hardness of the rubber and the frictional force are held constant. Moreover, wear caused by the somewhat softer IIR material in air is 20 to 50 times greater than that caused by other harder materials. Thus, chemical effects are clearly responsible for the different rates of wear.

One possible mechanism of chemical attack would arise from local heating during frictional sliding. Changes might occur in either the polymer or the metal as a result of pronounced temperature rises leading to enhanced wear. However, in nearly all cases the wear of steel was found to be much faster in an inert atmosphere than in air, proving that purely thermal or thermo-oxidative reactions are not the principal mechanisms of wear. Instead a general correlation can be drawn between the rate of metal wear and the degree to which long-lived free radicals are generated when the corresponding elastomer molecules are broken by a mechanical stress. This correlation is examined here in some detail, together with the effects of the surrounding atmosphere and the carbon black content of the rubber compound upon the rate of metal wear.

3.2. Radicals generated by molecular rupture

When uncross-linked polymers are subjected to severe mechanical shearing stresses, the molecules undergo homolytic scission producing pairs of highly reactive macromolecular free radicals [9]. Such species are known to take part in a variety of chemical reactions, depending upon their particular structure and reactivity and upon the reactivity of the surrounding medium. In some cases, e.g. polybutadiene, the radicals mainly take part in chain transfer reactions leading to bond restoration and continued cross-linking (gelation) [10]. In other cases, e.g. polyisobutylene [11] and poly(ethylene-co-propylene) [12] the radicals are mainly stabilized by H abstraction from other molecules, resulting in molecular breakdown. Furthermore, carbon radicals are highly reactive with oxygen, if present in the surrounding atmosphere, and thus peroxy radicals are formed in air [13]. This process also results in either cross-linking reactions or stabilization of the broken molecular ends.

3.3. Changes in abraded rubber particles

Measurements have been made of the equilibrium swelling in *n*-decane of particles of rubber wear debris. As shown in Table II, elastomers which undergo mainly radical scission reactions yield debris which swells more, or is completely soluble, in *n*-decane, whereas elastomers which undergo mainly radical cross-linking reactions yield debris which swells to about the same degree as the original material. Moreover, the changes found when wear takes place in a nitrogen atmosphere are in accord with the known mechano-chemistry of the corresponding uncross-linked polymer. For example, natural rubber (NR) is known to undergo molecular breakdown in air by reaction of the mechanically created radicals with oxygen. The original radicals are resonance-stabilized to some degree, however, and they are also sterically hindered from intermolecular reactions. Thus, in the absence of oxygen they undergo primarily combination reactions, maintaining the original molecular weight largely unaltered [9]. Correspondingly, the wear debris formed in air is severely degraded to a soluble tarry liquid whereas that formed in nitrogen retains its original rubbery appearance and resistance to swelling. On the other hand, it appears that EPR undergoes molecular rupture both in air and in nitrogen because the macromolecular radicals formed in this material are highly reactive and abstract hydrogen from other molecules, resulting in lower molecular weight products through disproportionation reactions [12]. The wear debris is degraded to a soluble tarry liquid, both in air and nitrogen, in accordance with this mechano-chemical feature of the base polymer.

TABLE II Linear swelling ratio for rubber debris swollen in decane at 25° C

Elastomer	New	Worn in air	Worn in N_2
SMR	1.3	Soluble	1.3
EPR	1.4	Soluble	Soluble
SBR	1.2	1.3	1.3
IIR	1.3	1.8	1.4
BR	1.2	1.2	1.2
TPR	1.4	1.4	1.4

Thus it appears that the network of elastomer molecules in tyre tread rubber undergoes occasional rupture under indentation and frictional forces during wear, producing pairs of highly reactive macromolecular free radicals that react in the same way as in the corresponding uncross-linked polymer.

Figure 3 Edge of a "Schick Plus Platinum" razor blade after abrasion against SBR in nitrogen. The direction of rubber motion is indicated by the arrow.

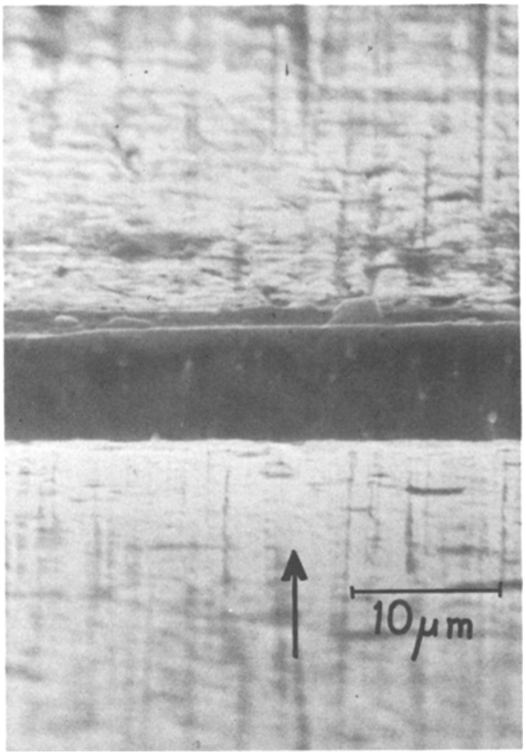

Figure 4 Edge of a "Schick Plus Platinum" razor blade after abrasion against TPR in nitrogen. The direction of rubber motion is indicated by the arrow.

3.4. Wear of steel

The rates of wear given in Table I suggest a general correlation between the propensity of an elastomer to bring about wear of steel and the life-time of the macromolecular carbon radical generated by frictional sliding. For example, the resonance-stabilized radicals formed in SBR and NR are particularly long-lived in nitrogen, and these materials cause particularly severe wear in nitrogen, as shown in Fig. 3. In contrast, the highly-reactive radicals formed in TPR, BR and EPR do not cause much wear of steel even in nitrogen, as shown in Fig. 4, presumably because they participate in internal reactions with other polymer molecules. In air, the radicals can react also with oxygen and the wear of steel is then extremely small for these polymers.

A number of questions are raised by these results. Is the wear caused by rubber associated in some way with the complexity of the alloy, for example with the carbon content of the steel? Does the hardness of the rubber affect the rate of wear of the metal? Is the wear resistance of the metal itself affected by the surrounding atmosphere? Some experiments designed to answer these questions, at least in part, are described in the remainder of this paper.

3.5. Wear of different metals

Rates of wear of three metal blades, worn against different rubber wheels, are given in Table III. For all the blades a softer wheel, based on SBR, is much more abrasive than harder wheels, based on BR, indicating again that chemical processes are primarily responsible for the differences in wear rate. Moreover, the effect is clearly not peculiar to razor-blade steel or carbon steel, it is even more evident for the non-ferrous blade, indicating that reaction with iron or carbon atoms is not the only mechanism of radical attack upon metals. The differences between the rates of wear for the three metals is more in accord with their different strengths, as measured by Rockwell hardness, rather than with known resistances to chemical attack. This suggests that the observed wear is brought about first by a chemical reaction with the metal and then by detachment of metal fragments, after reaction. The latter step will be

TABLE III Wear rate × 10^{16} ($m^3 rev^{-1}$) of various metals against BR and SBR rubber compounds

Wear conditions	Razor blade steel	Unalloyed steel	Aluminium–bronze alloy
BR-40 (Shore hardness 58)	0.05	–	2.8
BR (Shore hardness 66)	0.3	–	14.5
BR-60 (Shore hardness 73)	2.6	3.1	30.5
SBR-40 (Shore hardness 60)	16	21	1830
BR-60 (in nitrogen)	12.8	–	61

more difficult for harder and stronger metals.

It is noteworthy that wear rates of the bronze blade in nitrogen do not appear to be increased to the same degree as those for the stainless steel blade. This observation is discussed later in connection with possible effects of the atmosphere on the metal itself.

3.6. Effect of hardness of the rubber

A general correlation was found between the rate of wear of the metal blade and the hardness of the rubber compound it was worn against. Some results indicating the magnitude of this effect are given in Table III for compounds based on BR. These compounds yield dry powdery debris and do not undergo major changes in their physical state during wear. Polymers that undergo decomposition during wear, e.g. NR, IIR and EPR, also showed the same effect but in these cases the wearing surface becomes soft and sticky and the hardness of the original compound seems somewhat irrelevant.

Whether the pronounced effect of hardness of the rubber compound is due mainly to the increased amount of carbon black incorporated into the elastomer is not at all clear. Carbon black particles are hard and presumably abrasive, so that increasing the amount would lead to enhanced wear of the metal on this basis alone. However, in view of the striking correlation observed between wear rates of the metal blade and radical reactivities of the polymer molecules, it is clear that the elastomer is not acting solely as a carrier of abrasive particles of carbon black in causing wear of metal blades. Perhaps free radical species are formed at a greater rate in elastomer compounds containing larger amounts of carbon black. Alternatively, carbon black itself may play an important role in stabilizing polymeric radicals.

Further experiments are needed to separate the effects of carbon black from those of the elastomer itself. Unfortunately, compounds made harder by other means, for example, by increased cross-linking of the polymer molecules, are much weaker than carbon black-reinforced compounds and wear away so rapidly under large frictional forces that no detectable wear of the metal scraper is observed.

3.7. Effect of test atmosphere

The rate of wear of a steel scraper was increased by a large factor, between 5 and 50, when wear took place in a nitrogen atmosphere instead of in air (Tables I and III). The sole exception was with a butyl rubber (IIR) compound when the rate of wear decreased. This anomalous result is discussed later. Other experiments in argon and *in vacuo* gave the same rates of wear as in nitrogen, and established that the critical factor is the presence or absence of oxygen. It should be noted, however, that oxygen was not completely removed from the test chamber in any of these experiments. About 0.2% was estimated to be present in the nitrogen, argon and *in vacuo* experiments.

These striking changes in the rate of wear of steel blades in an inert atmosphere raise an important question: are they due mainly to the chemistry of polymeric radicals or are they due mainly to characteristics of the metal surface: for example, the presence or absence of an oxide layer? Although an oxide layer probably forms (or reforms) on the metal quite rapidly, even at low concentrations of oxygen in the test atmosphere, there are some indications that both the metal surface and the polymer reactivity are changed significantly in an inert atmosphere and are jointly responsible for the observed effects.

EPR is broken down to a liquid-like state by wear in air and in nitrogen because in either case the free-radicals formed by molecular rupture undergo hydrogen-abstraction and disproportionation reactions, causing further decomposition of the polymer [12]. In spite of this similarity in the physical and chemical changes, the wear of a steel blade is several times greater in nitrogen than in air (Table I). BR, on the other hand, tends to undergo further cross-linking in both air and nitrogen due to chain transfer reactions of the radicals formed [10]. Again, we note that the wear of a steel blade is much faster in nitrogen than in air, although the polymer undergoes rather similar physical and chemical changes in both cases. These observations suggest that the metal surface is more reactive towards polymeric radicals in an inert atmosphere, probably because of a reduction in, or absence of, an oxide layer in the wearing region. Nevertheless, the large differences observed in the relative wear rates in nitrogen and in air for various polymers shown in Table I, provide strong evidence for the importance of the chemical reactivity of the polymeric radical. For example, with NR the factor is approximately 50, whereas with IIR the factor is only about 0.3.

The unusual behaviour of IIR in an inert atmosphere is particularly interesting. Apparently the macro-radicals formed from this polymer in an inert atmosphere are themselves relatively stable, probably for steric reasons, and they react with steel to a marked degree. Peroxy radicals, formed by reaction of the original carbon radicals with oxygen in air, appear to be resonance-stabilized to a still greater degree and cause even more wear, in contrast to all the other polymers examined.

Measurements of the rate of wear of the bronze blade in a nitrogen atmosphere showed a relatively small increase, about two-fold (Table III). The smaller effect for this material may indicate a more reactive oxide layer or, alternatively, one more easily removed by abrasion.

4. Conclusions

The following conclusions have been reached.

(1) Rupture of rubber molecules to form macromolecular radicals takes place during abrasion.

(2) Subsequent reactions of these radicals are characteristic of the elastomer and of the presence or absence of oxygen. They may cause further molecular scission leading to decomposition of the rubber to a softer, liquid-like state, or they may take part in addition reactions leading to regeneration of the molecular network and further cross-linking.

(3) These polymeric radicals can also attack steel and other metals, causing wear by a combination of chemical reaction and detachment of metallic fragments. The efficiency of the wear process varies greatly with the elastomer that the metal slides against; it appears to be correlated with the stability of the polymeric radical. When the radical is highly reactive it takes part primarily in internal polymer reactions and causes relatively little wear of an abrading metal scraper. On the other hand, stable polymeric radicals appear to attack metals vigorously.

(4) In an inert atmosphere the rate of wear of a metal scraper is generally increased by a large factor, between 5 and 50 times, depending upon the elastomer against which the scraper slides. This striking effect is attributed mainly to the greater stability of carbon radicals, in general, in comparison with corresponding peroxy radicals, although some part of it probably also reflects a diminished oxide layer on the metal.

(5) In contrast, the rate of wear against butyl rubber (IIR) was found to be greater in air than in nitrogen, by a factor of about three. This anomalous behaviour is attributed to enhanced stability of the peroxy radical in this particular material, compared to the carbon radical formed by molecular rupture.

(6) Rates of wear of metal scrapers were found to increase markedly as the hardness of the rubber compound was increased by incorporating more carbon black. Although this effect is not unexpected, the mechanism has not yet been identified.

(7) There is clearly a need for detailed studies of the reactions of free radicals with metal surfaces and the role of mechanical activation. The present experiments suggest that such studies might lead to new metal finishing processes.

Appendix

The mix formulations in parts by weight and the vulcanization conditions used in preparing the rubber wheels were as follows:

BR*: *Cis* 1,4-polybutadiene (*cis* 4 1203, Phillips Petroleum Company), 100; N330 carbon black (Vulcan 3, Cabot Corporation), 50; pentachlorothiophenol (RPA No. 6, E. I. duPont de Nemours

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* When different amounts of carbon black were employed, e.g. 40 or 60 parts by weight, in place of the amounts indicated, the materials are denoted BR-40, BR-60, etc., in the text.

and Co), 0.07; zinc oxide, 5; stearic acid, 2; phenyl-β-naphthylamine, 2; Philrich HA5 oil (Phillips Petroleum Company), 7.5; sulphur, 0.5; Sulfasan R (Monsanto Chemical Company), 1.5; Santocure MOR (Monsanto Chemical Company), 1. Heated for 45 min at 146° C.

NR: Same as for BR, except *cis* 1,4-polyisoprene (Standard Malaysian Rubber 5L) in place of *cis* 1,4-polybutadiene. Heated for 35 min at 146° C.

TPR: Same as for BR, except *trans*-polypentenamer (supplied by Dr M. A. Golub, NASA Chemical Research Projects Office) in place of *cis* 1,4-polybutadiene. Heated for 45 min at 146° C.

*SBR**: Butadiene-styrene copolymer (75/25, FRS-1502, Firestone Tire and Rubber Company), 100; N330 carbon black (Vulcan 3, Cabot Corporation), 54; zinc oxide, 5; stearic acid, 2; phenyl-β-naphthylamine, 1; Santocure (Monsanto Chemical Company), 1; sulphur, 2. Heated for 60 min at 150° C.

IIR: Poly(isobutylene-*co*-isoprene) (98/2, Butyl 268, EXXON Chemical Company), 100; N330 carbon black (Vulcan 3, Cabot Corporation), 50; zinc oxide 5, stearic acid, 1; sulphur, 1.75; tetramethylthiuram disulphide, 1; mercaptobenzothiazole, 0.5. Heated for 30 min at 120° C, followed by 70 min at 150° C.

EPR: Poly(ethylene-*co*-propylene) (56/44, Vistalon 404, EXXON Chemical Company), 100; N330 carbon black (Vulcan 3, Cabot Corporation), 50; sulphur, 0.32; recrystallized dicumyl peroxide, 2.7. Heated for 30 min at 143° C, followed by 70 min at 160° C.

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