

Transfer of Copper and Zinc in Polymeric Materials Oxidized in Contact with Brass

D. G. LIN* and I. M. ELISEEVA

Department of Physics, F. Skorina State University, 246699 Gomel, Belarus

SYNOPSIS

Transfer particularities were investigated for zinc and copper in polymeric films oxidized in contact with brass. Inversion in selectivity of alloy component transfer proved to be the fact for a wide range of polymers. The results obtained are explained by an irregular development of oxidative transformations within the polymer layer, thus leading to a two-stage mode of transfer in the case of catalytically active metals. The influence of various factors (e.g., oxidation temperature, polymer film thickness, polymer origin) on the level of ultimate concentrations of copper and zinc accumulated in polymers was considered. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In previous articles¹⁻⁵ it was reported that oxidation of polymeric films in contact with brass had been accompanied by transfer and accumulation of the two alloyed components, copper and zinc, in the polymer bulk. Infrared (IR) spectra of the films¹ and polarographic analyses of the polymer sol residue²⁻⁴ evidenced accumulation of these metals. Research findings also indicated that in many cases relative concentrations of copper and zinc in the polymers would not equal their amounts in the alloy (i.e., selective dissolution of the metallic substrate took place).

The causes of selective transfer of brass components were not considered. The goal of the present work was to understand the peculiarities of copper and zinc transfer in polymeric materials oxidized in contact with brass by means of generalizing the results from the relevant literature and by attaining new experimental observations.

EXPERIMENTAL

The following materials were used in the experiments: unsaturated polymers such as natural rubber

(NR), synthetic isoprene rubber (SIR), synthetic butadiene rubber (SBR), synthetic butadiene nitrile rubber (SBNR-40 and SBNR-18), synthetic butadiene styrene rubber (SBSR), and saturated [e.g., polyethylene (PE)] carbon-chain polymers from which coatings were applied on metallic substrates.

The substrates were in the form of plates made from a brass alloy BR-63 and from one-component metals (viz., copper, CU-1, and zinc, Z-1). The coatings were oxidized in ovens in air, after which the polymeric films were separated from the substrates and examined. The degrees of oxidation and oxidative structurization (crosslinking) of the polymers were determined along with the concentrations of the metals (copper and zinc) found in them.

The oxidation level in the films was characterized by the extinction coefficient of the absorption band at 1720 cm^{-1} in the IR spectra of the polymers. The oxidative crosslinking of the polymeric material was estimated from the unsaturated fraction that remained after the specimen was exposed in the boiling solvent.⁶

The polarographic analysis⁷ was used to determine concentrations of the metals in the coatings. For this purpose a procedure was invented to determine simultaneously (from one sample) copper and zinc; the procedure implies ashing of the films, dissolution of the mineral residue in a background electrolyte, and subsequent polarography examination of the resultant solution. During the polar-

* To whom correspondence should be addressed at Department of Physics, F. Skorina State University 104, Sovetskaya Street, 246699 Gomel, Belarus.

ography procedure, copper concentration was determined first by using the ground electrolyte 1M HNO₃ (the reduction potential relative to the bottom mercury was 0.35 V); then the polarography procedure was repeated after the 1M aqueous solution was neutralized with an ammonia aqueous solution up to pH = 8.1 to 8.5 in order to estimate zinc concentration (the reduction potential was 1.2 V). The amounts of the metals were determined from the calibration plot constructed by using reference solutions.

The data presented in this article were obtained by processing statistically the results of as many tests as could provide an average error below 10%.

RESULTS AND DISCUSSION

Figure 1 exemplifies kinetic dependencies related to accumulation of carbonyl groups in PE¹ and SBR⁸ films oxidized on copper, zinc, and brass substrates. The substrate activity with respect to its influence on polymer oxidation as well as oxidative crosslinking decreased in this order: copper, brass, zinc. If PE films were oxidized in contact with brass or copper, there was an observed change from the polymer oxidation catalysis to oxidation inhibition, where carbonyl groups concentrations would get stabilized at a constant level (Fig. 1, curves 1 and 3). In PE films on brass, transition to inhibition takes place and the ultimate concentrations of carbonyl groups attributed to the inhibition period are higher. The kinetic dependencies of carbonyl group accumulation in PE films oxidized on zinc have only the period of oxidation catalysis (Fig. 1, curve 2).

Contact oxidation of polymers on brass was observed to be followed by dissolution and transfer in the film bulk of the two alloyed components^{3,8} (Fig. 2). However, their highest concentration in the films is lower than in the case of polymers oxidized on one-component substrates (Fig. 2, curves 1 to 4).

If compared to the concentration in the alloy, the components are accumulated in the polymeric films in an irregular manner. For example, Figure 2(b) shows data on NR contact oxidation. If the brass substrate had been dissolved uniformly, a similar relationship for zinc would have been represented by curve 7 in conformity with the kinetic dependence of copper accumulation (curve 5). The difference in the ordinates of curves 6 and 7 describes the selectivity in the component dissolution. In the initial period of NR film oxidation, copper was observed to have accumulated at a higher rate than zinc (curve 6 runs below curve 7). In the course of oxidation,

however, the transfer rate was noticed to increase for zinc, and there was a moment (t_0) when the relative concentration of brass components in NR films equaled the relative amounts of those components in the substrate. During subsequent contact oxidation of NR on brass (oxidation lasted longer than t_0), zinc was found to transfer in greater quantities (curve 7 runs above curve 6)—that is, in moment t_0 the dissolution selectivity of alloy components underwent inversion.

Inversion of selectivity in transfer of brass components has been supported experimentally for a wide series of polymeric materials. Figure 3 shows that the relative copper concentrations ($C_{Cu} : C_{Zn}$) in PE, SBR, SBNR-40, SBNR-18, NR, and SIR films varied with the oxidation time on brass. The dashed line stands for the level of initial relative concentration of copper in the brass substrate. The high relative concentration of copper in the film attained in the early oxidation period is shown to drop to values lower than the dashed line if the coatings were thermally treated further (i.e., inversion of selectivity took place in dissolution of the brass components).

The selective dissolution of copper and zinc changes the amounts of alloy components in the substrate surface layer. The data reported in a previous article³ showed that on the initial oxidation stage of NR films the relative concentration of copper in the brass substrate surface layer had decreased, probably due to the fact that copper had dissolved preferentially in the NR film. Later, the picture became reversed (i.e., the relative concentration of zinc in the substrate decreased due to its preferential transfer to the NR film).

Transfer of brass components to PE films was observed to discontinue at the stage of oxidation inhibition; the ultimate copper and zinc concentrations were reached simultaneously (Fig. 2, curves 2 and 4). It was only natural to think that zinc transfer was discontinued due to the fact that the brass surface had lost zinc through preferential dissolution in the oxidizing polymer. To verify this idea, a special experiment was conducted.

PE films were placed on copper plates and oxidized for a time length required to achieve the ultimate concentration of the metal in the film and inhibition onset. Then the films were separated from the substrates and arranged on zinc plates, and thermal treatment continued at a given temperature of oxidation. After this operation was completed, the concentrations of zinc and copper in the films were estimated. It appeared that zinc would not accumulate in the film (Fig. 4, curve 4). The experi-

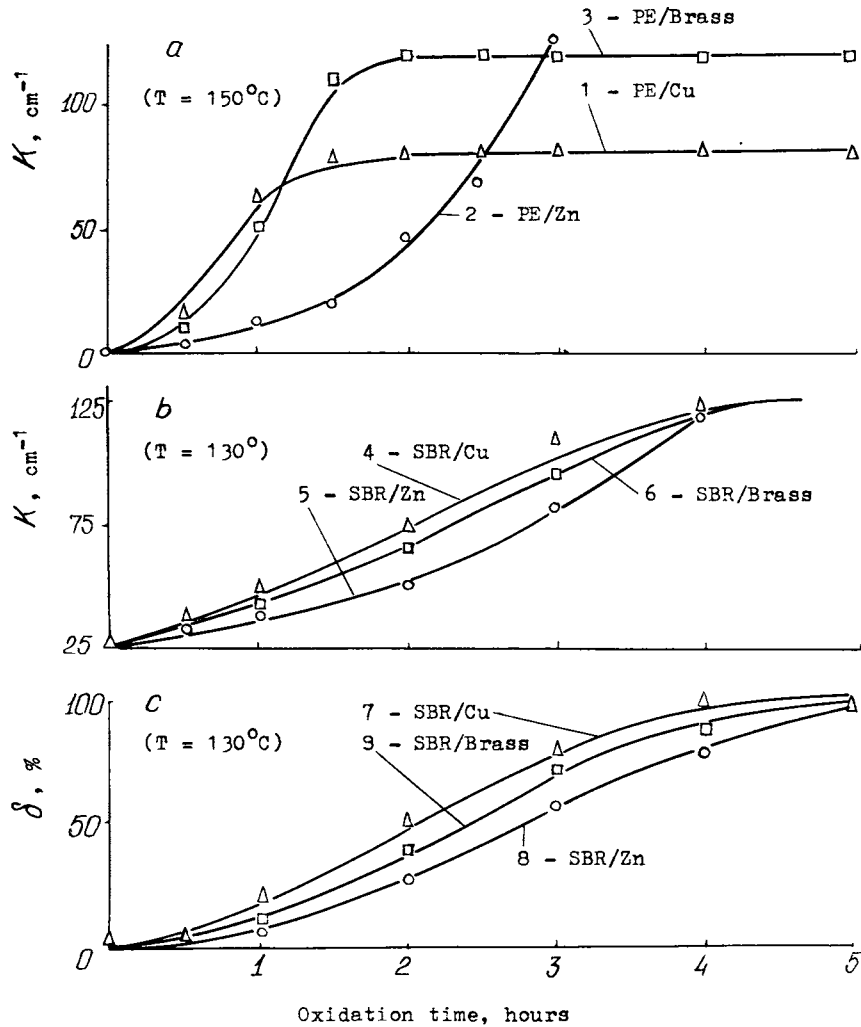


Figure 1 K is the extinction coefficient at 1720 cm^{-1} absorption band in IR spectra (a and b), and δ is the insoluble fraction (c) of polymeric films versus the oxidation time on copper, zinc, and brass substrates.

mental results made us believe that zinc transfer from the brass surface discontinued not because of a lower zinc concentration in the layer but because oxidation transformations in the PE film were specific (i.e., inhibition took place). If the alternation order of metals be changed for the reversed [i.e., first PE films are oxidized on zinc until the ultimate metal concentration is reached (oxidation inhibition would not occur in this case)], then on copper there will be a different result. At the stage of secondary thermal treatment of PE films, copper is accumulated up to a certain ultimate concentration (Fig. 4, curve 3). It was interesting to observe that ultimate copper concentrations in the preoxidized and unoxidized films appeared the same (Fig. 4, curves 2 and 3).

It is well known⁹ that polymer oxidation on catalytically active substrates begins directly in the region where the polymer touches the substrate and then gradually penetrates the bulk. This process is promoted by considerable oxygen penetration in the films and by diffusive transfer of metallic compounds catalyzing the oxidation process in the bulk polymer. Copper compounds could only be formed^{10,11} if oxygen had an easy access to the substrate to lead to metal's "disimprovement." In the absence of oxygen, or if there was an insufficient amount of it, copper could not chemisorb oxidation products, and no copper-containing compounds could be formed. Therefore, the initial stage of contact oxidation is characterized by severe transfer of copper compounds to the polymeric film.

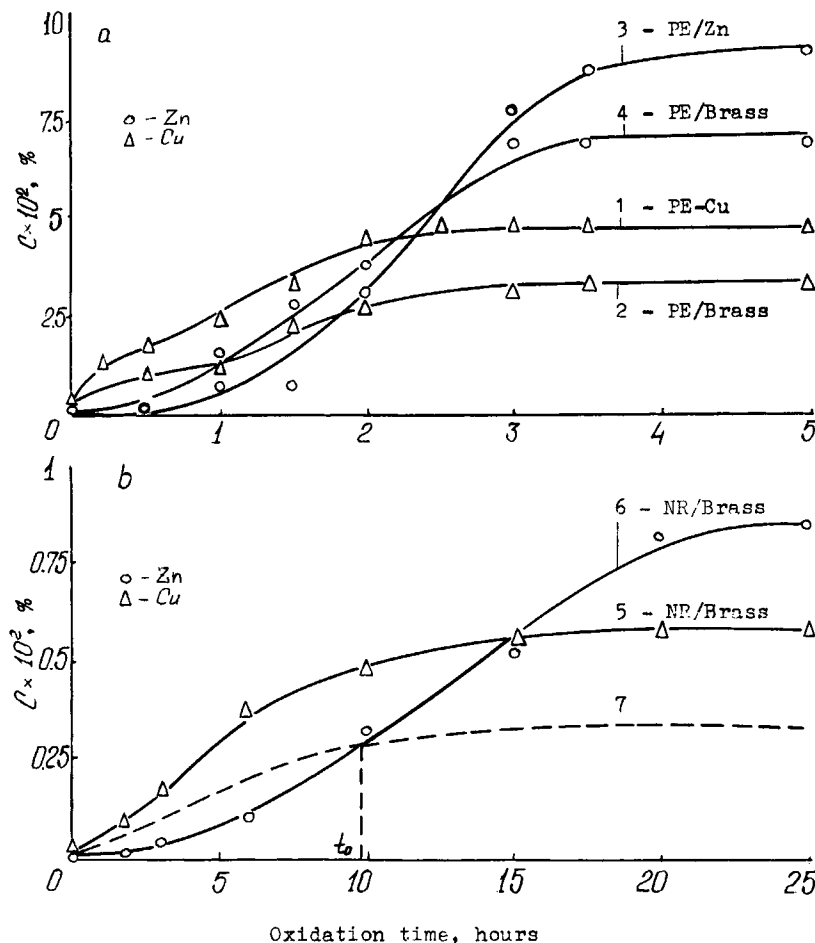


Figure 2 Copper and zinc concentrations in polymeric films versus the oxidation time at (a) 150°C and (b) 110°C on copper, zinc, and brass substrates. Solid line (—) corresponds to equal amounts of metals transferred from the substrate.

The development of oxidative transformations in the polymer/metal contact region is supposed to restrict oxygen diffusion; and after the induction oxidation period is completed in free films due to accelerated chemical bonding of the diffused oxygen in the coat surface layer, the oxidation process is localized in this layer.¹¹ Thus, two zones of severe oxidation occurring at different time periods can be found in the polymer coating¹²; they have opposite gradients in the products of the polymer oxidative transformation. The oxidation localization in the film's surface layer would lead to considerable amounts of low-molecular-weight products—resulting from thermal-oxidative degradation—which diffused into the coat volume and into the adhesion contact region. Interaction of these products and substrate results in a second stage of intensive formation of metal-containing compounds and causes metal to transfer into the polymer bulk. Figure 5, curve 1 represents data on metal accumulation in the

PE layer bordering on the copper substrate. Two stages of intensive metal accumulation separated by a period during which the metal concentration in PE layers would not in fact vary can be distinguished on the plot. The time separating the stages of severe copper accumulation in the polymer layer bordering on the substrate increases with the coat thickness (Fig. 5, curve 3). This can be explained by diffusive restrictions in the oxygen supply and oxidation products from the surface layer to the region of adhesion contact. At the same time, at the beginning of curve 3, Figure 5, there is a range of coat thicknesses for which metal is accumulated during one stage (the time period separating the stages is zero). In the present case, the time required to reach ultimate copper concentrations would not exceed the oxidation induction period for free films. Therefore, copper accumulation would be caused by oxidative processes developing in the layer neighboring the substrate; oxidation would not be displaced into the coat surface layer.

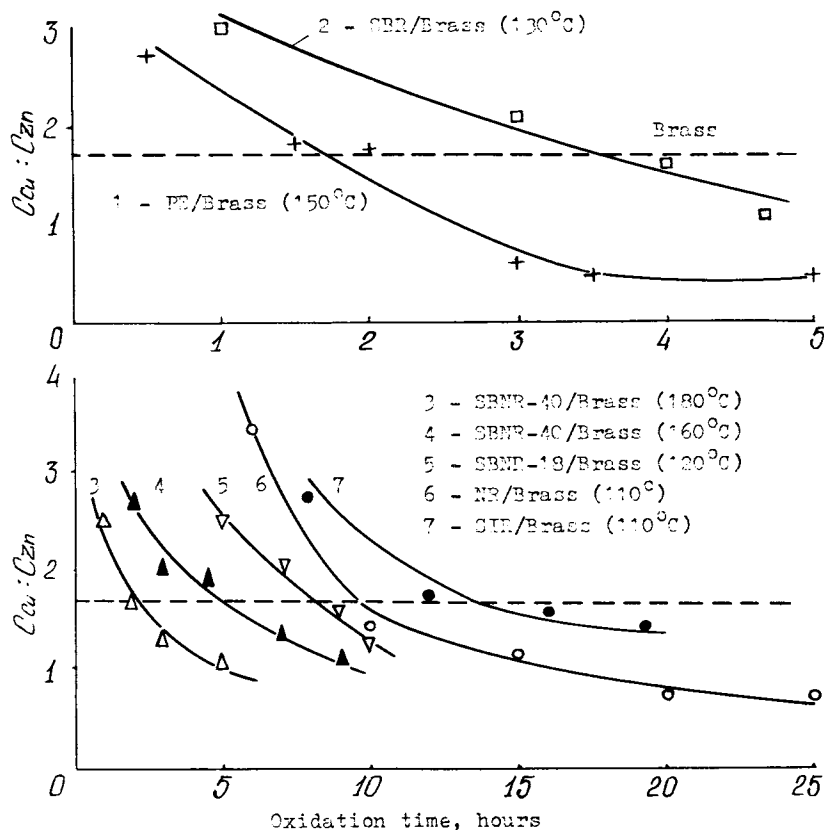


Figure 3 Copper concentration with respect to zinc in polymeric films versus the oxidation time on brass substrates.

The two-stage accumulation feature of copper could also be observed if polymeric films were oxidized on brass. This can be supported by data on copper transfer in PE films (Fig. 2, curve 2). Zinc would severely transfer in the film only after the oxidative process was shifted to the surface layer (Fig. 2, curve 4). At this stage oxygen would enter the region of adhesional contact to a limited extent; therefore, zinc acquires advantages in transfer, being a metal with a negative electrochemical potential.

Specific features of brass substrate surface layer structure participate in selectivity inversion of the alloy components' dissolution. Van Ooij et al. reported¹³⁻¹⁵ that very thin (0.5 nm) copper oxide films are found on brass coat surface; beneath those films a zinc oxide layer (10 nm) is found containing copper inclusions. It is clear that such an arrangement of brass substrate favors transfer of copper at the initial oxidation stage.

Oxidative transformations occurring in the coat surface layer led to both low-molecular-weight products of thermal oxidative degradation and oxidative crosslinking of macromolecules. As the crosslinking continues, the concentration of low-

molecular-weight products drops sharply, and metal transfer in the film decelerates up to complete termination. This can be supported, for example, by

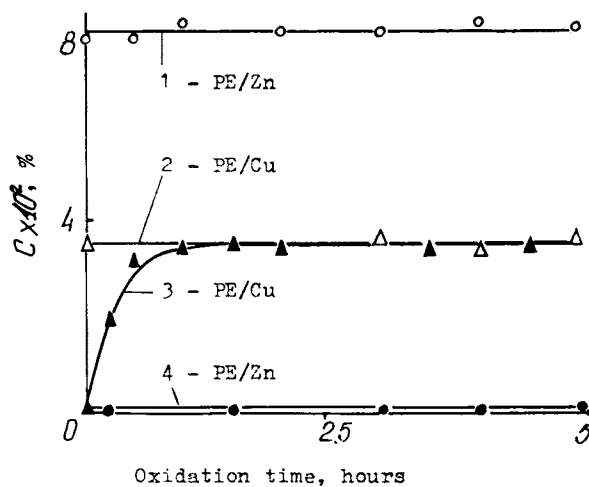


Figure 4 Copper and zinc concentrations in films preoxidized on copper (Δ) and zinc (\circ) versus subsequent oxidation time at 150°C on zinc (\bullet) and copper (\blacktriangle) substrates.

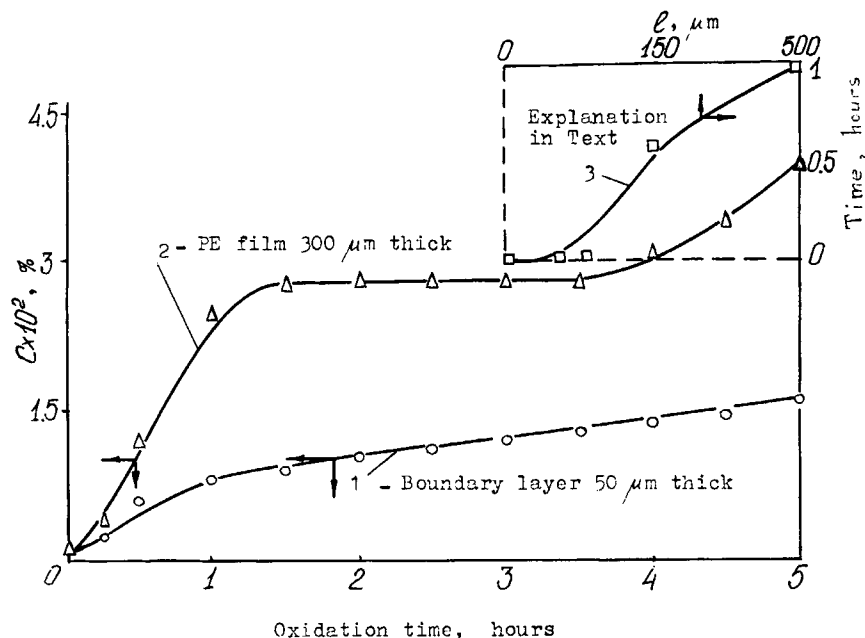


Figure 5 Copper concentration in PE films versus the oxidation time at 140°C on copper.

the research findings related to contact oxidation of SBSR films on metals.¹⁶ It is stated in that article that in addition to rubber crosslinking (insoluble fraction made 100%), the metal concentration in the film became constant.

The ultimate concentration of brass components transferred into polymeric films was noted to depend on a number of factors, primary of which are the oxidation temperature, polymer film thickness, and polymer origin. Figure 6 presents data on the effect of oxidation temperature on transfer of brass components in PE films in the following coordinates: copper concentration (C_{Cu}) and zinc concentration (C_{Zn}). The C_{Cu} - C_{Zn} curves were plotted by reconstructing the kinetic relationships related to the alloy components accumulated in the film. In the reconstruction, those portions of the relationships were used which represented relatively high metal concentrations. Equal alloy components' transfer corresponds to the relationship $C_{Cu} = C_0 \cdot C_{Zn}$ (Fig. 6, curve 4), where C_0 is the copper concentration in the alloy with respect to zinc. The deviation of the C_{Cu} - C_{Zn} curve from the $C_{Cu} = C_0 \cdot C_{Zn}$ curve indicates dissolution selectivity for alloy components. If the C_{Cu} - C_{Zn} curve runs above, copper is accumulated most; if it runs below, zinc is accumulated most.

Depending on the oxidation temperature, two situations are possible (Fig. 6): (1) prevailing copper transfer into the film (low oxidation temperature, curve 1), or (2) in the course of oxidation, transition from an excessive copper concentration in the film

to an excessive zinc concentration (higher oxidation temperatures, curves 2 and 3). The latter situation demonstrates the selectivity inversion in alloy components' transfer. With increasing temperature, the concentration of copper transferred to the film at the initial oxidation stage decreased. This can be explained by the fact that with temperature increase the induction period of oxidation, in the case of unbacked film, decreases, and as a result the duration and depth of oxidative transformations taking place in the polymer layer bordering on the substrate decrease. As noted earlier, the second accumulation stage for metals is due to interaction of the substrate and oxidation products formed in the coat surface layer; now zinc transfers from brass in greater amounts. This situation can usually be observed in reality (Fig. 6, curves 2 and 3).

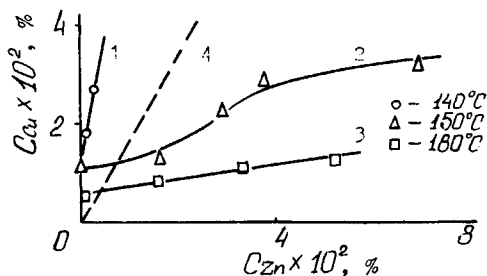


Figure 6 Copper concentration in PE films oxidized on brass substrates versus zinc concentration in the films. Solid line (—) corresponds to equal amounts of metals transferred from the substrate.

At rather high temperatures (the induction period for unbacked film oxidation is zero), the situation can be realized in which the polymer oxidizes only in the surface layer and there will be no first stage of metal accumulation with prevailing copper transfer (copper concentration in the film is within the measurement error on the initial oxidation stage).

An opposite effect was observed at low oxidation temperatures (Fig. 6, curve 1). Because of a long induction period of free film oxidation, oxidation localizes generally in the coat layer bordering on the substrate; the first accumulation stage for alloy components is realized with prevailing copper transfer. Copper compounds, while diffusing into the polymeric film, catalyze the oxidation process; the oxidation reaction front moves toward the outer coat surface to reach it. The coat volume thus gets saturated with copper-containing compounds (i.e., products of contact reactions). In earlier papers^{10,17-19} it was reported that copper compounds caused a dual influence on polymer oxidation: At low concentrations they acted as catalysts, whereas at concentrations exceeding a critical value those copper compounds inhibited the polymer oxidation process. Such behavior was typical of both copper compounds added purposely to the polymers and those that resulted from interaction of the substrate and polymer oxidation products. In the case of polymer contact oxidation on copper or on copper-containing substrates, the amount of copper compounds transferred into the film increased; after some ultimate concentration was reached, there was a transition from catalysis to inhibition (autoinhibition).²⁰ Such a transition has been proved experimentally for PE and Pentaplast²⁰⁻²² and can be seen in Figure 1, curves 1 and 3. Since the major amount of metals transfers in the course of polymer oxidation,¹¹ transition to oxidation inhibition in PE films on brass leads in fact to complete termination of copper and zinc transfer to the film. Therefore, transfer of brass compounds under mild conditions (low oxidation temperatures) was in fact restricted by the first accumulation stage of metals for which, as indicated earlier, copper transfer prevailed.

Under the isothermal conditions of oxidation, the ultimate concentration of copper compounds can be reached later the thicker the coat film. Therefore, by increasing the film thickness a one-stage accumulation mechanism for brass components can be changed to a two-stage one. In this sense, an increase in coat thickness is equivalent to an increase in oxidation temperature (i.e., a direct temperature-thickness analogy is observed in its influence on the transfer mechanism for brass components).

Table I Approximate Accumulation Levels of Brass Components in Polymeric Films (50 to 200 μm thick) Oxidized in Contact with Alloy

Polymer	Concentration ($\% \cdot 10^{-2}$)	
	Copper	Zinc
PE	3-4	6-7
SBNR-40	0.8-1	0.3-0.4
SBNR-18	0.7-0.8	0.4-0.5
SBR	0.5-0.6	0.5-0.6
NR	0.5-0.6	0.8-0.9
SIR	0.5-0.6	0.8-0.9
SBSR	0.08-0.09	0.02-0.03

All materials tested were supplied by Russian companies.

As mentioned earlier, transfer of brass components depends on the polymer origin. Table I lists data on the ultimate level of copper and zinc accumulated in polymeric films oxidized in contact with brass. Since the data were obtained under dissimilar experimental conditions (different time-temperature regimes, different film thicknesses), they should be treated as tentative. Nevertheless, Table I shows that the accumulation level for copper and zinc in saturated polymers (e.g., PE) exceeds significantly the figures for unsaturated polymers. This can be explained by a negative effect on the metal transfer: oxidative crosslinking taking place in rubbers at high rates. As a result, no ultimate concentration of copper-containing compounds could usually be reached if rubbers were oxidized on copper or copper-containing substrates; no explicit transition from catalysis to inhibition of oxidation was observed. The oxidized rubbers investigated can be arranged, in view of diminishing activity toward accumulation of copper compounds, as follows: SBNR-40, SBNR-18, (SBR, NR, and SIR have approximately equal activities), and SBSR. Copper levels in SBNR-40 and SBSR differ by one order of magnitude. Higher activities of rubbers containing amide groups, unlike hydrocarbon rubbers, are typical of saturated polymers as well (e.g., polycapramide).

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