

TECHNICAL APPROACHES TO IMPROVING THE SCRATCH RESISTANCE OF TPO'S PART I: SURFACE LUBRICATION

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Abstract

The present paper provides a review of the scientific and patent literature concerning the effects of migratory and nonmigratory surface lubricants in enhancing the scratch resistance of polypropylene-based materials. The advantages and disadvantages of these additives are discussed. The use of coadditives to moderate the migratory behavior of some slip additives is also considered.

Some migratory slip additives have been known to produce stickiness on the surface of parts after weathering, which presents a concern for the entire automotive supply chain. A theoretical model is presented relating this phenomenon to slip additive migration and photodegradation, which is in good agreement with previously reported results showing the effects of slip additive concentration and the type of hindered amine light stabilizer used in the formulation.

Introduction

Improving the scratch resistance and surface durability of polypropylene and TPO used for automotive interior and exterior parts continues to be a topic of interest to the industry. Over the years a number of technical approaches have been developed which provide varying degrees of improvement in scratch resistance. Examples include increasing part surface lubricity through the use of slip additives (*e.g.* fatty acid amides and siloxanes), filler selection (*e.g.* wollastonite vs. talc), improving adhesion between the polymer matrix and inorganic fillers (*e.g.* through surface modification and compatibilization), and increasing surface hardness (*e.g.* through polymer architecture as well as the use of additives such as nucleating agents).

One particular strategy that has been successfully employed to reduce scratch damage in polypropylene-based materials is to lubricate the surface using slip additives. As the coefficient of friction at the surface is reduced, the magnitude of the maximum tensile stress during scratching is also decreased, which in turn reduces brittle scratch damage such as cracking, crazing, and cavitation.[1] Decreasing the coefficient of friction has also been shown to reduce the yielded zone size on the surface from scratching, resulting in reduced scratch visibility.[1]

Slip additives may be categorized as migratory or nonmigratory. Migratory slip additives must migrate from the bulk of the part to the surface in order to function as lubricants. Nonmigratory slip additives are by their nature randomly distributed throughout the part, and must be used at relatively high concentrations in order for enough additive to be present at the surface to provide a lubricating effect.

Migratory Slip Additives

Primary and secondary fatty acid amides are the most common migratory slip additives, including oleamide, erucamide, stearyl erucamide, ethylene bis(oleamide), and oleyl palmitamide (Figure 1). The use of these additives to reduce the coefficient of friction at polymer surfaces has been practiced since the 1950's, when they were first employed in polyethylene films.[2] The products

function by migrating from the polymer bulk to the part surface to form a close-packed, oriented layer (Figure 2).[3] In polyethylene, a monolayer of the additive has been shown to be sufficient to reduce the coefficient of friction to a low value.[4] In polypropylene films, migratory slip additives can provide a reduction in the coefficient of friction from about 0.9 to less than 0.2.[5]

Figure 1. Examples of Migratory Slip Additives.

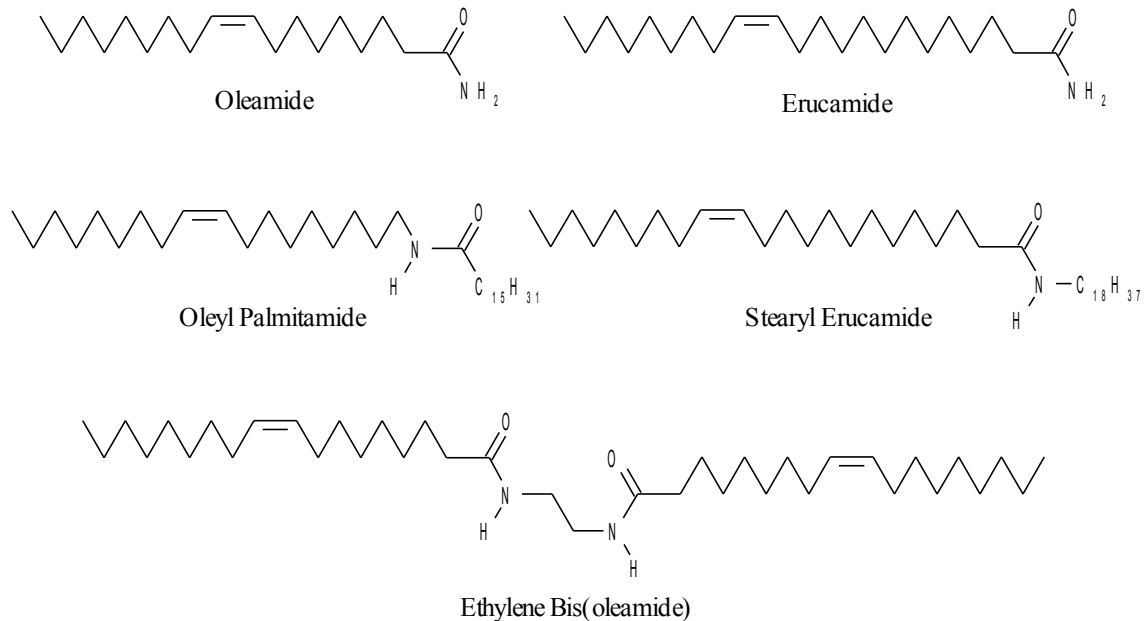
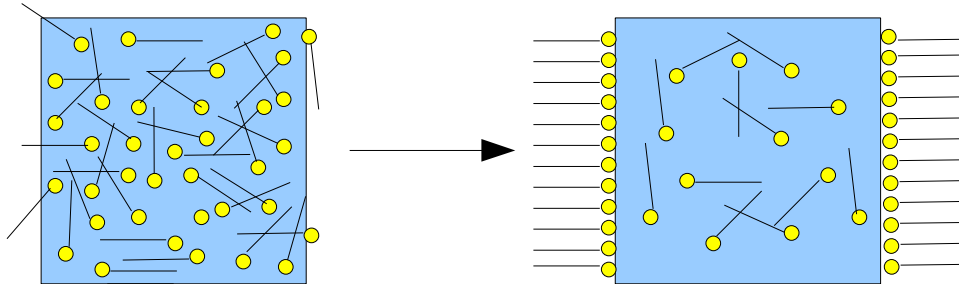


Figure 2. Migration of Slip Additives to Form a Lubricating Monolayer.



Adapted from Reference 3

One consequence of the migratory nature of these additives is that some time (hours to days) may be required after molding for the lubricating layer to form on the part surface.[6] The time required is dependent on a number of factors, including the concentration[3] and molecular weight[5,6] of the additive, the part thickness,[3] the nature of the polymer substrate, and the influence of other formulation components. It has also been speculated that enrichment of the additive concentration at or near the surface may result from contact of the polymer melt with metal mold surfaces having a high surface energy.[3,7]

In nonpolar substrates like polyolefins, the oriented lubricating layer is very weakly bound to the polymer surface and can be disrupted by exposure to humidity and heat[3] as well as by physically wiping the surface. Maintaining surface protection over time requires that molecules of the slip additive continually migrate from the bulk layers of the part to the surface to replace

molecules that are lost.[4] The permanence of the effect can be enhanced by depositing multiple layers of slip additive at the surface[4] or by introducing polar functionality to the polymer surface to enable a stronger interaction with the polar amide “head” of the slip additive.[3] However, the fact remains that surface protection is temporary as at some point during the lifetime of the article all of the slip additive will be depleted.

For rough or textured surfaces, migratory slip additives have been shown to coalesce along surface features. After prolonged storage, the filling in of hollows in the surface by slip additives has been observed.[8] For these types of surfaces, the effect of slip additives on the coefficient of friction is complex and is dependent upon the degree of roughness, the direction of contact relative to the surface grain, and the applied load.[4] In general, the effect of slip additives in reducing the coefficient of friction (and hence improving scratch resistance) is greater for smooth surfaces than for rough ones. However, some types of grained surfaces have also been suggested to provide inherently improved scratch resistance.[9]

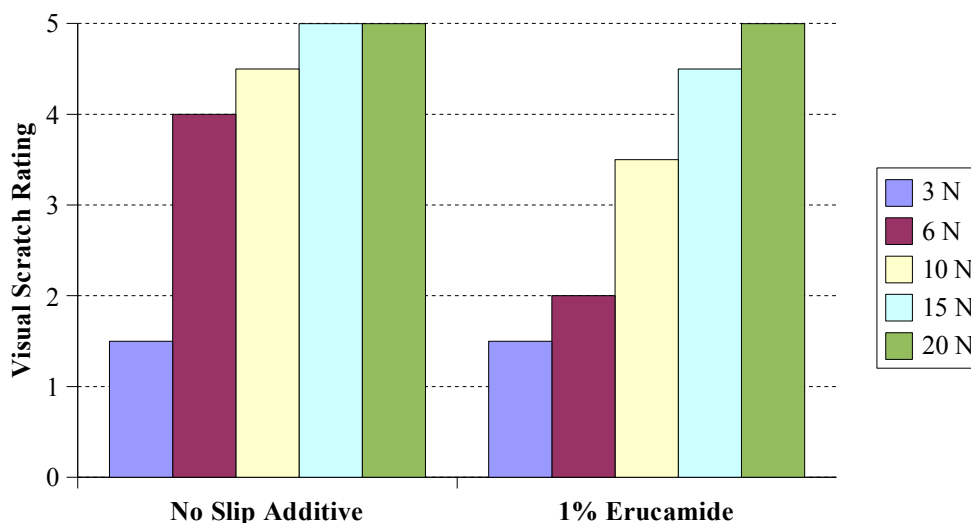
As expected from their effect on the coefficient of friction, migratory slip additives improve the scratch resistance of unfilled and talc-filled TPO compounds. Table 1 illustrates the improvement of scratch resistance in an unfilled TPO compound using erucamide and oleamide as measured by the Ford 5-finger scratch test.[10] Scratch resistance was also improved in talc-filled compounds as shown in Figures 3 (Ford 5-finger scratch test),[11] and 4 (increasing load at constant scratch speed).[12]

Table 1. Effect of Migratory Slip Additives on Scratch Resistance in an Unfilled TPO Compound.

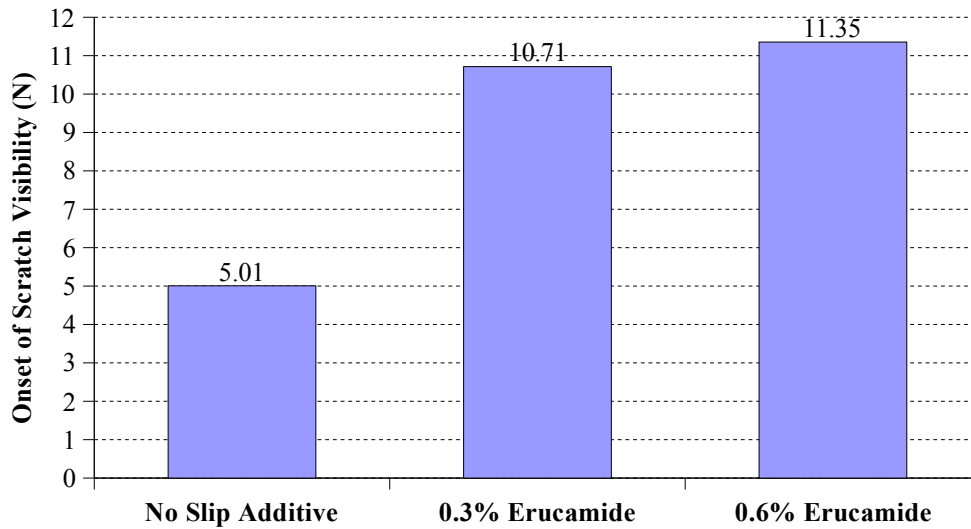
Slip Additive	Force to Give Visible Scratch
None	0.6 N
0.3% Erucamide	>7 N
0.3% Oleamide	>7 N

Substrate: 50% PP homopolymer, 50% ethylene-butene copolymer/PP blend, 4 phr carbon black
 Scratch Testing: Ford Test Method BN 108-13
 Data from Reference 10

Figure 3. Effect of Erucamide on Scratch Resistance in a Talc-Filled TPO Compound.



Substrate: 20% talc-filled PP copolymer containing carbon black
 Scratch testing: Ford Five Finger Scratch Test
 Data from Reference 11

Figure 4. Effect of Erucamide on Scratch Resistance in a Talc-Filled TPO Compound.

Substrate: 20% talc (untreated) filled PP/EPR copolymer containing carbon black
 Scratch Testing: ASTM D 7027-05
 Data from Reference 12

Nonmigratory Slip Additives

High molecular weight polysiloxanes are the most common nonmigratory slip additives used to enhance the scratch resistance of polypropylene-based materials.[13] The nonmigratory slip additives have some technical advantages over their migratory counterparts. For example, they provide an immediate and somewhat more durable antiscratch effect (for example after washing) and are less prone to blooming. Also owing to their nonmigratory nature they would be expected to be evenly distributed at the surface, even in textured parts. A major disadvantage vs. migratory slip additives is inferior cost performance due to both the higher price of the additive and the higher loadings that must be used to give an effect at the part surface.[11] It has also been reported that polysiloxanes have are prone to adsorption on talc, which necessitates the passivation of the talc filler (for example by pretreatment with an epoxy resin) prior to incorporation of the polysiloxane.[14-16] Many polysiloxanes are viscous liquids, which can be difficult to handle and dose in a compounding operation. For this reason more user-friendly solid forms such as masterbatches have been developed and are typically employed.

The effect of a polysiloxane vs. migratory slip additives on the scratch resistance in an unfilled TPO compound is shown in Table 2.[10] In the unwashed test specimens, the polysiloxane provides scratch resistance approaching that of oleamide and erucamide. However, unlike the migratory slip additives, the polysiloxane shows no decrease in performance after washing.

Combinations of migratory and nonmigratory slip additives have also been employed.[10,14] This approach enables the use of lower loadings of the more expensive polysiloxane while providing a more durable antiscratch effect than when migratory slip additives are used alone.

The antiscratch performance of combinations of polydimethylsiloxane (PDMS) and erucamide in a talc-filled polypropylene compound are shown in Table 3.[14] In all of the examples except one the talc surface was passivated by the addition of epoxy resin prior to adding PDMS. The results show that the level of PDMS can indeed be reduced without compromising scratch resistance by partial substitution of erucamide. The beneficial effect of passivating the talc surface prior to adding the PDMS is also apparent.

The effect of combinations of polysiloxane and amide slip additives in an unfilled TPO compound is shown in Table 4.[10] These compositions provide good scratch resistance before and after washing.

Table 2. Effect of Slip Additives on Scratch Resistance in an Unfilled TPO Compound Before and After Washing.

Slip Additive	Force to Give Visible Scratch	
	Before Washing	After Washing
None	0.6 N	0.6 N
0.2% Oleamide	>7 N	0.6 N
0.2% Erucamide	>7 N	0.6 N
2% Siloxane Masterbatch (50% Active)	6 N	6 N

Substrate: 50% PP homopolymer, 50% ethylene-butene copolymer/PP blend, 4 phr carbon black

Scratch Testing: Ford Test Method BN 108-13

Data from Reference 10

Table 3. Effect of Slip Additive Combinations on Scratch Resistance in a Talc-Filled PP Copolymer.

Slip Additives	Scratch Ranking
None	12
2% PDMS	1
2% PDMS*	7
1% PDMS	9
1.5% PDMS	9
1% PDMS + 0.5% Erucamide	5
1.5% PDMS + 0.5% Erucamide	1

Substrate: 22% Talc-filled PP medium impact copolymer

Talc Passivation: 0.5% epoxy resin added prior to PDMS except where indicated (*)

Scratch Testing: Hand-operated scratch tester, up to 1 kg weight, 0.5 mm stylus, visual assessment

Data from Reference 14

Table 4. Effect of Slip Additive Combinations on Scratch Resistance in an Unfilled TPO Compound.

Slip Additive	Force to Give Visible Scratch	
	Before Washing	After Washing
None	0.6 N	0.6 N
2% Siloxane Masterbatch	6 N	6 N
0.2% Erucamide 0.2% Oleamide	>7 N	2 N
2% Siloxane Masterbatch 0.2% Erucamide 0.2% Oleamide	>7 N	>7 N

Substrate: 50% PP homopolymer, 50% ethylene-butene copolymer/PP blend, 4 phr carbon black

Scratch Testing: Ford Test Method BN 108-13

Data from Reference 10

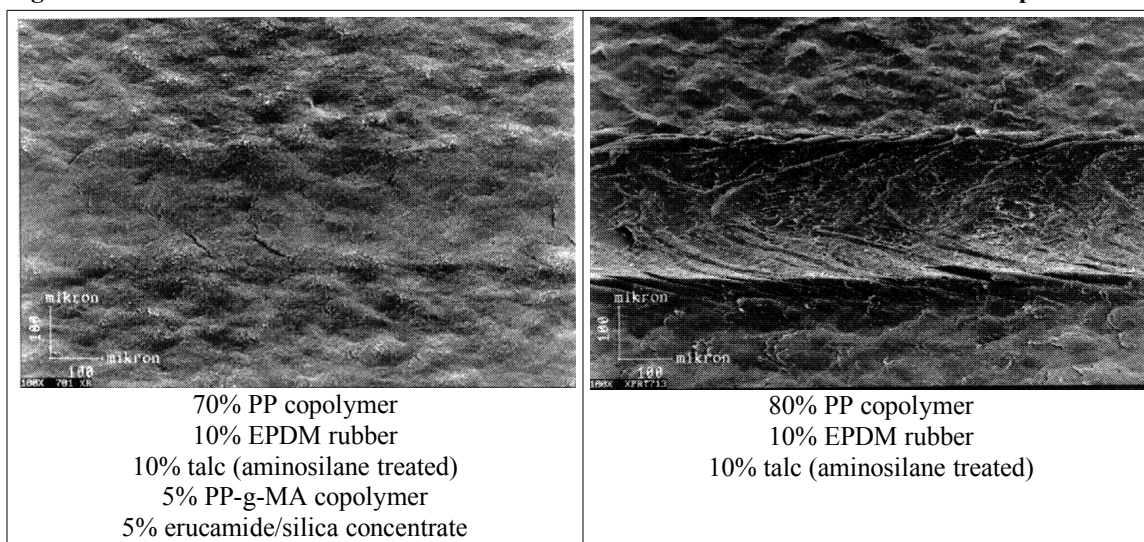
Coadditives to Improve the Performance of Migratory Slip Additives

Migratory slip additives represent a powerful tool to enhance the scratch resistance of polypropylene-based materials. The best features of these additives include their effectiveness in reducing the coefficient of friction at part surfaces, excellent cost performance, and ease of incorporation during plastic compounding operations. However, there are also a number of drawbacks to use associated with their migratory nature.[11] These include a tendency towards excessive migration sometimes resulting in visible exudation of the additive on the surface (“blooming”), the transient nature of the lubricating effect (“lag time” before onset of the effect as well as its inherent lack of permanence), uneven distribution on textured surfaces, contribution to automotive fogging, and part stickiness sometimes observed after weathering.[17]

It has long been known that slip additive migration and solubility are influenced by the polarity of the substrate. For example, in polyethylene films it is known that including a polar ethylene-vinyl acetate copolymer (EVA) as a blend stock increases the solubility and slows the migration of amide slip additives.[18] Similar strategies have been successfully employed to reduce slip additive migration in polypropylene-based substrates. For example, additive compositions comprising amide slip additives, EVA, and other components have been employed to improve the scratch resistance of talc filled TPO.[19] Combinations of amide slip additives with polyolefin graft copolymers containing polar segments (*e.g.* polyacrylate) have also been shown to provide excellent scratch resistance with superior resistance to blooming vs. the same slip additive used without the graft copolymer.[20] Copolymers of long-chain α -olefins with maleic anhydride which have been functionalized with long chain alcohols or amines have also been proposed as coadditives.[21-23]

The main mechanism by which these organic coadditives improve slip additive solubility and reduce migration probably involves hydrogen bonding between the polar amide “head” of the slip additive and hydrogen bond acceptors such as carbonyl groups in the nonmigratory coadditive.[18] The possibility also exists that the polar coadditive may surface segregate to a degree during molding, providing polar functional groups at the surface to which the polar amide “head” of the slip additive can attach by hydrogen bonding, thus increasing the permanence of the antiscratch effect. Besides the coadditives that have been mentioned, it is likely that other copolymers which are compatible with polypropylene and also contain polar functional groups will also be effective to increase the solubility of amide slip additives and reduce the undesired effects of excessive migration.

Inorganic materials such as synthetic silicas can also be considered as coadditives for migratory slip additives. In LDPE films, the use of amide slip additives adsorbed on silica has been shown to provide a lower coefficient of friction vs. the amide slip used alone.[24] Most interestingly, the same workers reported that in polypropylene films these additive compositions provided an immediate reduction in the coefficient of friction after extrusion, whereas the same amide slip additive used alone required several days to produce the desired effect. Compositions comprising these additives and other components have also demonstrated excellent scratch resistance in talc-filled TPO (Figure 5).[25] More recently, more advanced silica-slip additive compositions with improved form and handling properties have been developed.[26]

Figure 5. Effect of Additive Combination on Scratch Resistance in a Talc-Filled TPO Compound.

Scratch testing: Ericsson pen according to ISO 1518
Photos from Reference 25

Migratory Slip Additives and Part Stickiness

One special technical issue associated with migratory slip additives that has recently been described is the potential for the formation of a sticky exudate after parts have been exposed to natural or accelerated weathering.[17]

Amide slip additives contain carbon-carbon double bonds. The allylic carbon atoms adjacent to these double bonds are particularly vulnerable to thermal and photochemical oxidation. The thermal oxidation chemistry of these slip additives has been described.[27] Photo-oxidation of amide slip additives appears to produce primary oxidation products which are responsible for the stickiness. As weathering continues, the primary oxidation products continue to degrade and are eventually broken down to low molecular weight species which are lost from the surface by volatilization. At the same time, the slip additive continues to migrate to the surface from the deeper layers of the part, but the rate of replenishment diminishes with time as the bulk concentration is depleted.

The duration of part stickiness after weathering can be understood using a qualitative theoretical model taking into account the photodegradation rate of the additive and the rate of additive replenishment at the surface by migration. A key point is that part stickiness after weathering is inherently a transient phenomenon, persisting until the rate of slip additive degradation exceeds the rate of its replenishment by migration. Based on this model the duration of stickiness is also expected to be concentration dependent, with the duration of stickiness increasing with the concentration. This is illustrated in Figure 6, where at the highest additive concentration (blue curve) stickiness begins to disappear at a later time (t_2) than at a lower additive concentration (red curve, t_1). If the additive concentration is sufficiently low, stickiness may be avoided altogether as degradation of the additive takes place faster than its replenishment (green curve). The predictions of the model are consistent with Solera and Sharma's observations (Figure 7).[17]

Figure 6. Qualitative Model: Effect of Slip Additive Concentration on Duration of Stickiness.

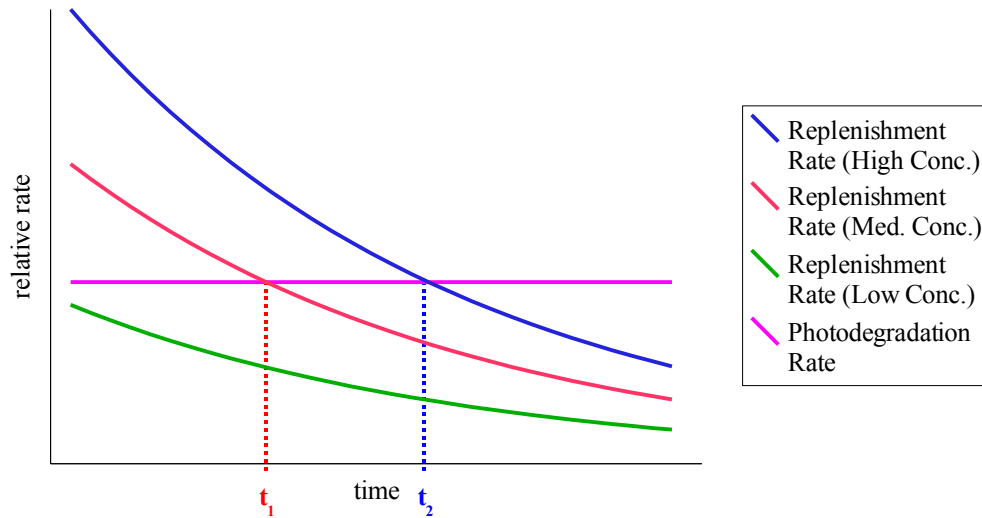
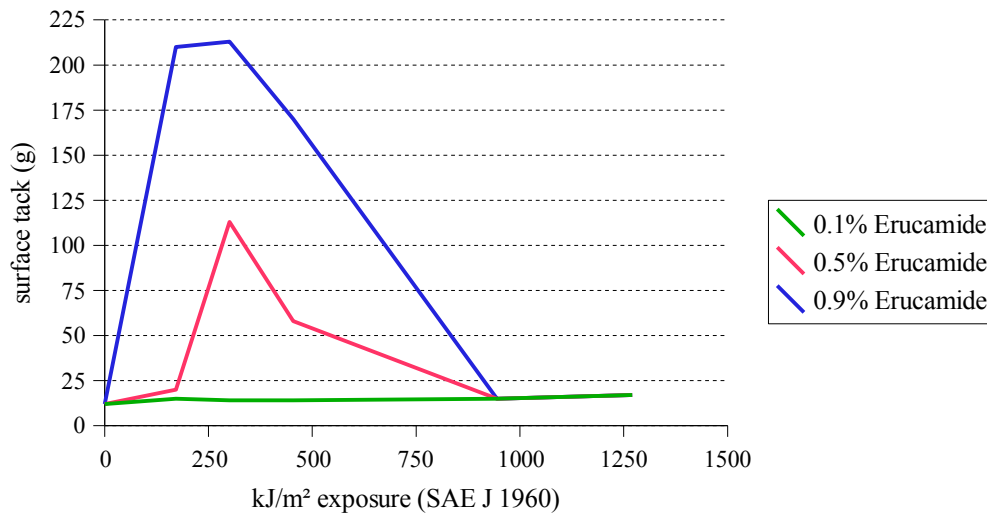
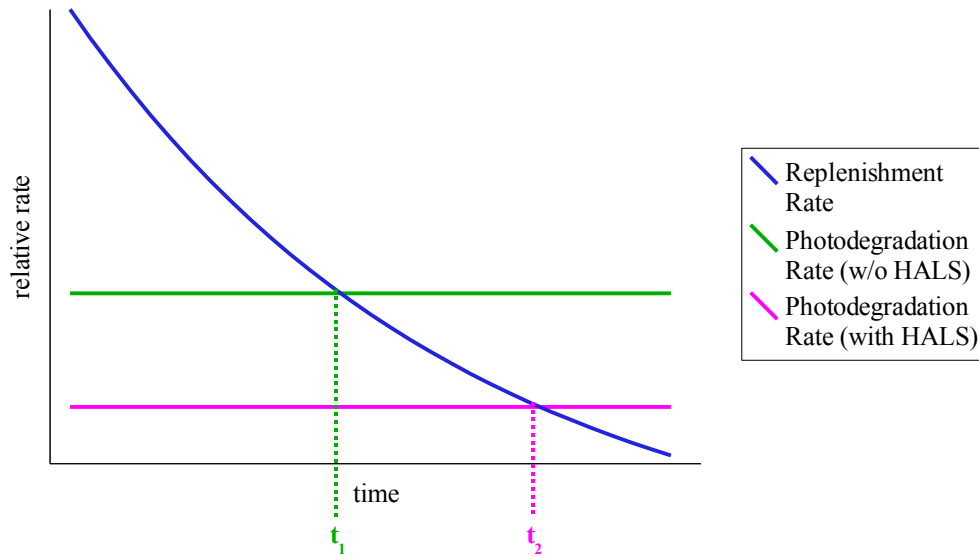
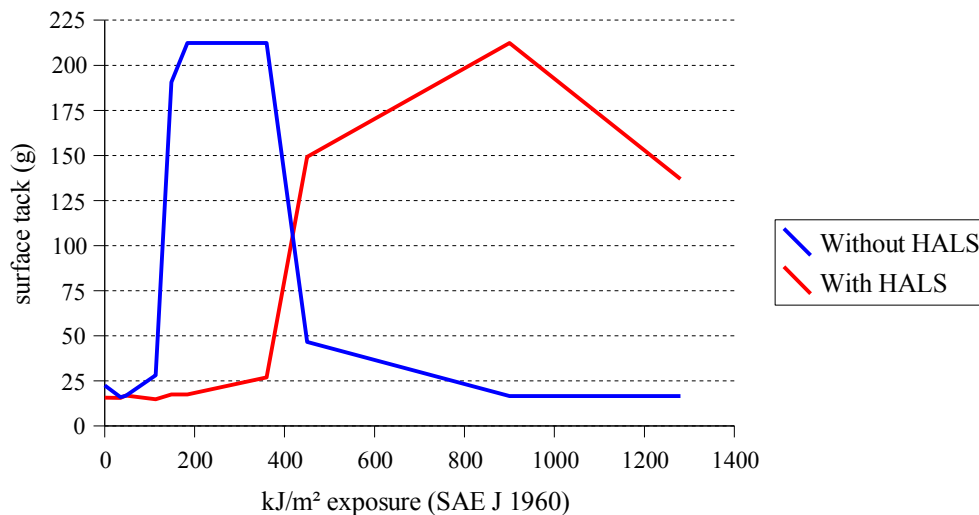


Figure 7. Effect of Erucamide Concentration on the Development of Surface Tack after Weathering.



Adapted from Reference 17

The type of light stabilizer used in the formulation has been shown to have a strong influence on the phenomenon.[17] The low molecular weight hindered amine light stabilizers (HALS) commonly used for TPO stabilization would be expected to migrate to the surface along with the slip additive, where they would reduce the rate of slip additive degradation and delay the onset of stickiness. However, once the sticky primary oxidation products have formed, the duration of stickiness would be extended because their degradation to volatile products is also inhibited. This is illustrated in Figure 8, where without added light stabilizer stickiness begins to disappear at earlier time (t_1) vs. when a low molecular weight, migratory HALS is present in the formulation (t_2). Again, the predictions of the model are consistent with Solera and Sharma's results (Figure 9).[17]

Figure 8. Qualitative Model: Effect of HALS on the Duration of Stickiness.**Figure 9. Effect of Hindered Amine Light Stabilizers on the Development of Surface Tack after Weathering.**

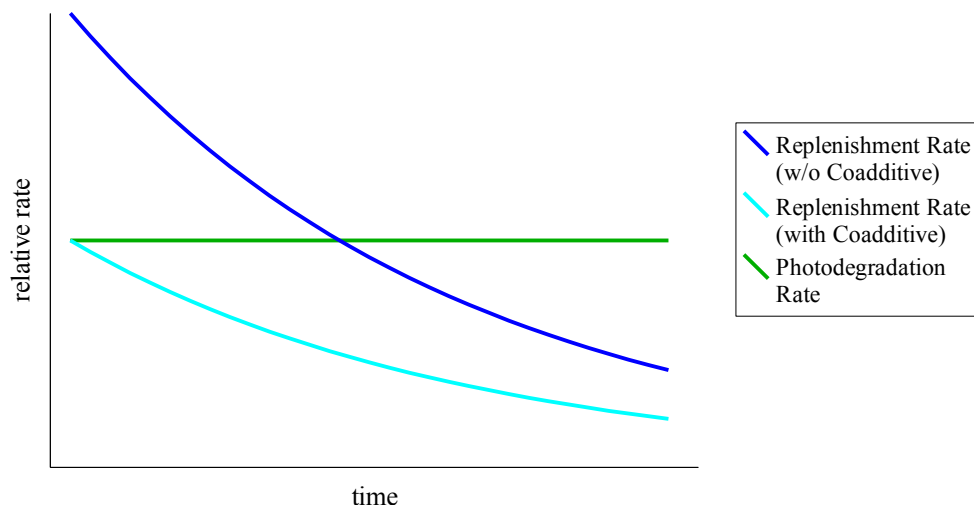
Adapted from Reference 17

According to the model, coadditives that reduce the migration rate of slip additives are expected to reduce the duration of stickiness. If the photodegradation rate of the slip additive is faster than the replenishment rate, it should be possible to avoid stickiness after weathering altogether (Figure 10, light blue line). This has been observed in practice for combinations of secondary amide slip additives with functionalized copolymers of long-chain α -olefins with maleic anhydride.[22]

Other formulation components such as fillers have been demonstrated to influence the oxidative stability of amide slip additives and may also play a role in the stickiness phenomenon. For example, it has been found that the thermal oxidative stability of erucamide in the presence of inorganic antiblock additives is related to the basicity of the filler as well as the presence of transition metal oxide impurities such as iron oxide.[28] In that study, the more acidic synthetic silicas provided the best oxidative stability, followed by neutral to slightly basic talcs, then the

more strongly basic diatomaceous earths (which also contained the highest concentration of iron). It would be interesting to assess the effects of talc pH, transition metal content, and surface treatment on the stickiness phenomenon.

Figure 10. Qualitative Model: Effect of Coadditive on the Duration of Stickiness.



Conclusions and the Potential for Technical Improvements

Systems based on migratory slip additives provide some improvement in the scratch resistance of polypropylene-based materials, but improvements may still be desired in the absolute level of scratch resistance that can be attained as well as the permanence of the effect and elimination of the potential for stickiness during the part lifetime. Further improvement of scratch resistance could be accomplished by the development of a higher performance slip additive capable of reducing the coefficient of friction at the part surface to a greater extent than state-of-the-art slip additives such as erucamide. On the other hand, the poor oxidation stability of conventional slip additives appears to be responsible for the stickiness after weathering phenomenon. The latter issue could be addressed by the development of more oxidation-resistant slip additives. The migratory characteristics of a new slip additive could also be optimized in product design by tailoring the molecular weight.

Potential also exists for improvement of coadditive technologies. A compatible but surface-segregating polar coadditive could improve the permanence of the surface lubricating effect by providing hydrogen-bonding sites at the surface for amide slip additives.

Nonmigratory slip additives such as polysiloxanes overcome some of the disadvantages of the migratory additives. However, these additives suffer from problems such as inferior cost performance and interactions with talc fillers. Improvements needed to improve the viability of this approach include additive cost reduction and also improved technology for passivating talc surfaces.

Final Words

The patent status of particular additives, combinations of additives, and their use in specific polymers, formulations, and applications can be very complex. When developing new formulations, it is recommended to conduct a thorough search of the literature to avoid infringement of any valid patents. When in doubt seek legal counsel.

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