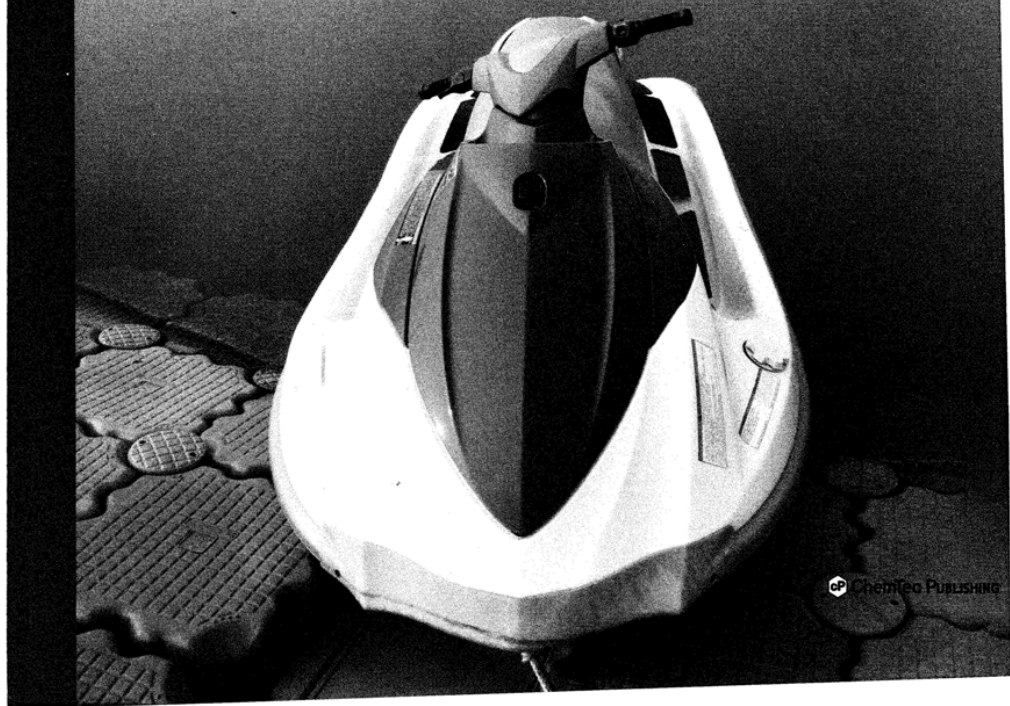


Third Edition

Handbook of **ANTIBLOCKING, RELEASE, and SLIP ADDITIVES**

George Wypych



Handbook of
**Antiblocking, Release,
and Slip Additives**
3rd Edition

George Wypych



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ally not relevant for blocking since blocking occurs between materials of the same kind, whereas static charge formation occurs when different materials are separated.¹⁰

Surface energy was already shown to affect the chemical structure of surface layers. In theories of adhesion, the work of adhesion between two identical surfaces is given by this equation:¹⁰

$$W_c = 2\gamma_s \quad [5.3]$$

where:

γ_s surface energy.

This simple equation does not play any important role in the prediction of blocking phenomenon. The knowledge of surface energy of components of formulation helps to predict the tendency of components to migration.

One of the practical remedies used to reduce blocking is to cover blocking substances with a layer which prevents blocking. This method is frequently used in plasticized PVC in which plasticizer migration causes between-layer-adhesion. This adhesion can be easily eliminated by kiss-coating with lacquers (e.g., films, coated fabrics, etc.).¹¹

The above discussion shows that blocking phenomena may be caused and remediated by many physical and chemical principles. The remedial action obviously depends on the reasons which created the problem. In general terms, the most likely mechanism of action of an antiblocking agent is through either of the two actions:

- prevention of migration and residence on the surface of materials that may cause between-layer adhesion (most frequently, these are low molecular weight polymeric materials, plasticizers, etc.)
- migration of materials which reside on surface but do not cause between-layer adhesion.

The above mechanism seems overly complicated but it reflects the complex nature of action of various additives. Figures 5.4 and 5.5 demonstrate this complex nature of actions of different additives. It is common to use a combination of two or more additives; for example, antiblocking and slip additive. Such a combination may include, for example, fatty acid amide and silica. Fatty acid amide will more likely be named as a slip agent and silica will most likely be named an antiblocking agent. In the case of oleamide, silica acts as an antiblocking agent and it decreases blocking force relative to its concentration. It does not affect antiblocking performance of stearamide, which is much more effective in antiblocking than silica. Silica concentration does not affect the coefficient of friction of oleamide, which is very low regardless of silica concentration. In this combination of oleamide and silica, silica is the antiblocking additive and oleamide is the slip agent. Silica reduces the coefficient of friction of films containing stearamide. In this

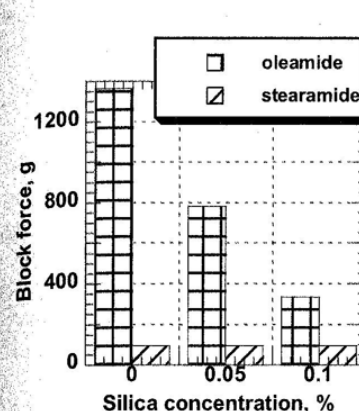


Figure 5.4. Effect of antiblocking silica agent on block force for polyethylene films containing 0.1% of stearamide or oleamide. [Data from Horne, S. E.; Suarez, J. J., *SPE J.*, **25**, 11, 34-8, 1969.]

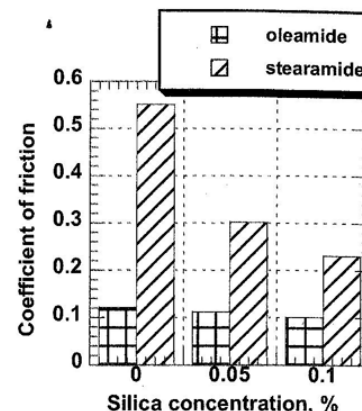


Figure 5.5. Effect of antiblocking silica agent on coefficient of friction of polyethylene films containing 0.1% of stearamide or oleamide. [Data from Horne, S. E.; Suarez, J. J., *SPE J.*, **25**, 11, 34-8, 1969.]

combination of stearamide and silica, silica acts as the slip agent and stearamide as the antiblocking agent. It is evident from the above example that

- additives used in combination may support each other's action (or help to reduce each other's deficiencies)
- depending on the combination, a role of additive may change (a commonly known antiblocking agent may become a slip agent, and *vice versa*).

Proper dispersion of antiblocking agent is considered important for efficiency of its action. Agglomeration of antiblock and its insufficient dispersion decreases its influence on antiblocking properties of film.³⁰ Particle size is also important, considering that large particles cause defects in films and other materials and thus reduce mechanical performance of the product. At the same time, the surface area of larger particles is smaller and therefore they have reduced capacity of adsorbing low molecular weight substances, which is one of the prerequisites of their good performance.

5.2 SLIP AGENTS

The previous section revealed that the primary function of a slip additive is to reduce the coefficient of friction. Also, the chemical group of fatty amides briefly discussed in the previous section consists of the most popular slip additives used by industry. Their mechanism of action is understood. Figures 5.6 and 5.7 illustrate two most important aspects of this mechanism.

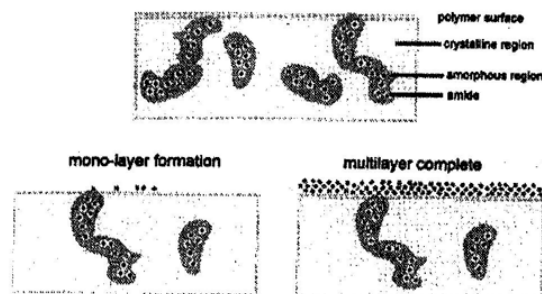


Figure 5.6. Distribution of slip agent in melt and formed product. [Adapted, by permission, from Coupland, K.; Maltby, A. J.; Parker, D. A., AddCon Asia '97, International Plastics Additives and Modifiers Conference, Singapore, Oct. 28-29, 1997, paper 15, 1-5.]

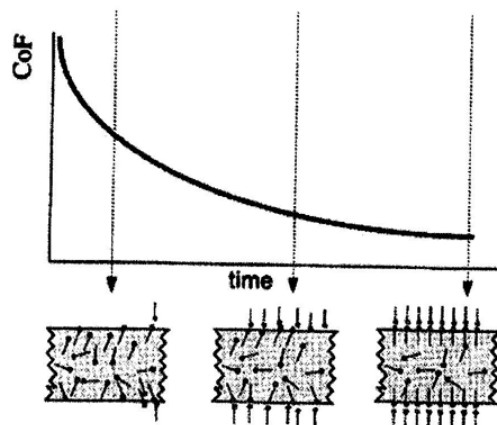


Figure 5.7. Surface orientation of slip agent and its effect on coefficient of friction. [Adapted, by permission, from Coupland, K.; Maltby, A. J.; Parker, D. A., AddCon Asia '97, International Plastics Additives and Modifiers Conference, Singapore, Oct. 28-29, 1997, paper 15, 1-5.]

elements: an amide group and a hydrocarbon chain. The hydrocarbon chain has high affinity to polyethylene, which has very similar properties, and for this reason hydrocarbon chains in the first layer are embedded in polymer with their amide groups facing air. When more slip agent molecules arrive on the surface, they form the second layer on the surface. The molecules of the second layer orient themselves with amide groups facing each other. This is again natural, consid-

Figure 5.6 shows that when a slip agent is mixed with polymer melt, it is absorbed into the polymer amorphous regions where it resides until the polymeric material is in the form of a melt. On cooling, the slip additive becomes incompatible because of its different surface energy and it begins its journey to the material surface. The rate of migration depends on the difference between the surface energies of the polymer and the additive (the larger the difference, the faster the migration). First, a monolayer is formed on the polymer surface, followed by deposition of subsequent layers when new molecules of antislip agent arrive on the surface.

Figure 5.7 shows that the arrangement of molecules on the surface is not chaotic but it has a structure which results from the affinity of two segments contained in the slip agent. Fatty amides that are described by this mechanism have two structural

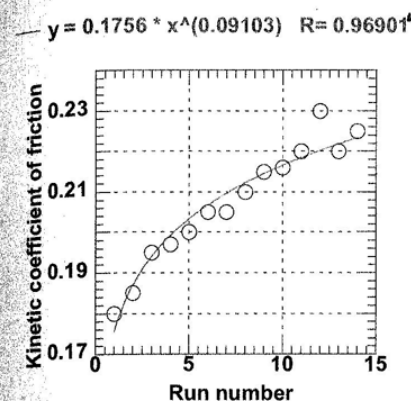


Figure 5.8. Kinetic coefficient of friction of polyethylene film containing erucamide after contacting metal element in each run without cleaning. [Data from Janorkar, A. V.; Hirt, D. E.; Wooster, J. J., *Polym. Eng. Sci.*, **44**, 1, 34-44, 2004.]

films contact many metal rollers and guides, which may affect the distribution of slip agent on the surface. Detailed studies were conducted for erucamide in polyethylene and polyolefin plastomers.^{15,16} Figure 5.8 shows the results of an experiment in which polyethylene film containing 1,200 ppm of erucamide was contacted with a metal plate, and after each contact, the coefficient of friction was measured. The coefficient of friction increases after each run but the magnitudes of the increases are gradually diminishing. This prompted proposal of a mechanism explained in Figure 5.9. Film contact with equipment removes some slip agent from the film surface but accumulation of slip agent on a surface of metal parts eventually results in slip agent transfer to the film surface and slip agent loss gradually diminishes.^{15,16}

Films are subjected to winding pressures during production and storage. The effect of pressure on slip agent migration is an essential element of the mechanism of its action.^{17,18} The results of studies are not conclusive yet. It was observed that

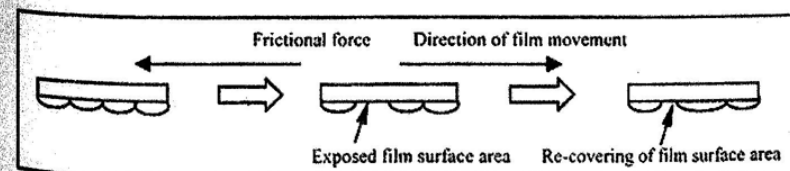


Figure 5.9. Mechanism of coating replenishment during contact of surface of polymer film with mechanical elements of line. [Adapted, by permission from Janorkar, A. V.; Hirt, D. E.; Wooster, J. J., *Polym. Eng. Sci.*, **44**, 1, 34-44, 2004.]

at high pressures exerted on a film, the amount of slip agent found on the surface decreased. If films were stacked and pressure was applied to the films, the amount of slip agent on the surface increased compared to individual films. It was also found^{17,18} that slip agent preferentially migrated to a film/film interface compared with film/air and film/teflon interfaces. This is consistent with the observations on stacked and single films but still it is difficult to explain why less slip agent migrates to the surface when pressure increases. There seems to be a critical pressure over which diffusion of slip agent decreases. Below this critical pressure, no effect of pressure on diffusion process is observed. Incorporation of additive leads to its uniform distribution in the material bulk but additive may then effectively migrate to the surface, resulting in uniform distribution on the film surface.¹⁹

Rate of migration is an essential factor and it depends, among other things, on chemical structure. It was found by XPS spectroscopy that the surface concentration of oleamide was increasing for 30 days until it become constant.²⁰ Stearamide, at this point of time, had 3 times lower concentration on the surface than oleamide. Oleamide undergoes surface oxidation due to the presence of double bonds in its structure.²⁰

It is noticeable that the above mechanism is based on studies of fatty acid amides while other slip agents are also used for various purposes related with reduction of coefficient of friction. Fluoropolymer additives, for example, are used to improve film extrusion in which they act in a similar manner during process as amides act in the final film.²¹ Fluoropolymer additive is also not compatible with polymer matrix. During extrusion, it migrates to the surface of metal and forms a film which has a pronounced effect on production parameters. It reduces melt fraction, viscosity, shear rate, and gate pressure. This makes production faster and energy use lower. Some of these additives are developed in such a manner that they migrate only in a molten state but are immobilized within material after it solidifies. This makes them essentially absent from the film surface, which in some post-process operations is an important requirement.²¹

From the above explanations, it becomes obvious that performance of slip additives depends on their compatibility with matrix and diffusion phenomena. Both are quite well understood from the theoretical point of view but much less from the point of view of application of theories to complex systems in which additives work. These systems contain many different additives which compete with themselves and affect each other's performance (including compatibility and diffusivity so important for the performance of slip agents).

5.3 RELEASE AGENTS

In order to select a suitable release agent, the reasons for adhesion must be known. Adhesion is caused by four mechanisms, including:²²

- mechanical interlocking
- interdiffusion
- surface absorption and reaction
- electrostatic attraction.

In compliance with these mechanisms of adhesion, it is essential that a release agent has these properties:²³

- an affinity to or a bond formation with the mold surface but no compatibility with the molded part
- chemical inertness to both the mold and the molded part
- good wetting characteristics of the mold material to form a continuous film on the surface
- insolubility in the material being molded
- heat resistance to process temperatures
- resistance to other factors that may cause adhesion, such as formation of static charges or adhesion between glossy surfaces.

The above points show that in spite of the fact that release properties are seemingly easy to understand, the multiplicity of causes demands a complex set of properties from a suitable release agent. Also, the mechanism is described by a variety of influences falling into four categories listed in the beginning of this section.

Mechanical interlocking depends on surface finish of the mold (its original surface roughness). It also depends on mold wear properties. Figure 5.10 shows that surface roughness of untreated molds rapidly increases, but if mold is coated with triazine dithiol containing perfluorinated groups, the mold retains its original qualities for a long time.²⁴ The mold properties may also be affected by a release agent used. Figure 5.11 shows residue buildup, which depends on release agent type.²⁵

In summary, the original surface quality of a mold, its resistance to wear, and potential for modification of the mold surface by release agent, may affect the effectiveness of the release agent and the quality of products manufactured.

The interdiffusion in a three-layer system (mold-release-molded part) that may affect adhesion of the molded part would be a rather rare and unexpected development. Only absorption of release agent into the molded part may be considered here, and if the timing of this process is not suitable, then the performance of the release agent may suffer.

The release properties depend on surface absorption of molded material on a mold and reactivity of the molded material with the mold material. This can be expressed by work of adhesion and friction force, both acting to increase adhesion. Work of adhesion is given by the equation:²⁴

$$\Delta W = \gamma_p + \gamma_m + \gamma_{mp} \quad [5.4]$$

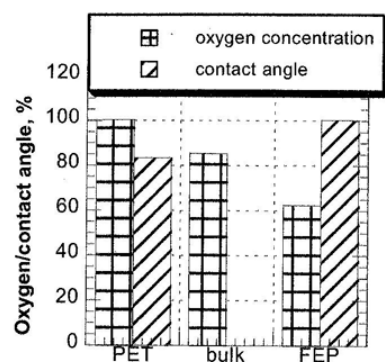


Figure 5.13. Relative oxygen concentration (PET=100%) and relative water contact angle (FEP=100%) for EAA, formed on the surface of PET and FEP molds and in bulk. [Data from Chihani, T.; Bergmark, P.; Flodin, P., *J. Adhesion Sci. Technol.*, 7, 4, 327-41, 1993.]

It is also possible that such material may interact with other materials in the formulation and modify their properties.

Polyethylene-poly(ethylene-propylene) diblock copolymer, PE-b-PEP, was studied as an additive to long chain paraffin oils, improving their properties, and assisting recovery and processing of waxy crude oils.⁵ The diblock copolymer, PE-b-PEP, self-assembles in oil to modify gel properties of paraffin. A small addition of PE-b-PEP (500 ppm) reduces yield stress of gel by factor of 3,000. The deposition of modified wax on a pipe wall forms a thin insulating layer which prevents further gel formation. The insulating later prevents cooling of the core liquid, which readily flows without blocking the pipes.

Reactive groups on the surface of molds may react with suitable groups in the processed material. For example, isocyanate groups readily react with hydroxyl groups found on the surfaces of many metals. It is also possible that the metal surface will have a catalytic effect on reactions on the surface and will make modification of surface properties of materials. Reflection spectroscopy in the IR region showed that the chemical properties of the metal walls of molds used to form polyurethane articles have an effect on the reaction of diisocyanates contacting the walls. In the manufacture of polyurethane moldings from polyols and diisocyanates, polyurea formation in the boundary layer or in directly adjacent materials represents a concurrent reaction to the polyurethane formative reaction. Urea formation depends on the metal; Cu promoted the reaction, which, however, proceeded slowly on polished Ti surfaces. The metal-specific chemical reactions

mold material the surface of material may be tailored to requirements. It should be noted that if molding occurs in the presence of a mold release agent, the surface of molded part will be modified according to the interaction between mold the release agent and melted polymer.

Polymer brushes are frequently discussed in literature. They are composed of a lamellar core and free chains forming a brush. If such material is included in composition and it diffuses into its surface layers, it may form properties related to the properties of brush chains and this could be one option of material design having high reactivity towards some adhesive, or with non-reactive, antiblocking surface.

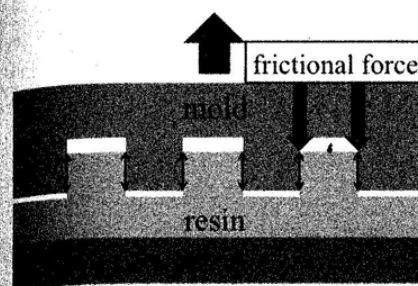


Figure 5.14. Diagram illustrating importance of friction between mold and cured resin. [Adapted, by permission, from Okada, M.; Yamashita, D.; Unno, N.; Taniguchi, J., *Microelectronic Eng.*, 123, 117-20, 2014.

in or on the phase boundary were also related to the mold release forces.⁸

Defect analysis and lifetime evaluation of release-coated nanoprint molds shows importance of friction between the mold and cured resin, which occurs mainly on the side walls of the mold (Figure 5.14).³¹ If release compound has a low frictional coefficient, such release agent will help to suppress the generation of errors and increase reliability of release mold coating.³¹

The above discussion shows that the mechanism of action of release agents is still a work in progress. Only

some influences can be described today, and this does not consist of unified mechanisms which can be used to predict potential improvements or problems that may be encountered with new materials.

REFERENCES

- Murphy, J., **Additives for Plastics Handbook**, Chapter 17: Lubricants, mould release agents, slip, anti-block, Elsevier, Oxford, 1996.
- Sobottka R.; Feltham E., Anti-blocking of Polymer Films in **Plastics Additives - An A-Z reference**, Ed. Pritchard, G., Kluwer 1998.
- Koromminga, T.; van Esche, G., **Plastics Additives Handbook**, Zweifel, H., Ed., Hanser, 2001.
- Horne, S. E.; Suarez, J. J., *SPE J.*, 25, 11, 34-8, 1969.
- Ashbaugh, H. S.; Fetters, L. J.; Adamson, D. H.; Prud'homme, R. K., *J. Rheology*, 46, 4, 763-76, 2002.
- Berry, A. K.; Bogan, L. E.; Agostine, S. E., *Ceramic Trans.*, 62, 125-32, 1996.
- Chihani, T.; Bergmark, P.; Flodin, P., *J. Adhesion Sci. Technol.*, 7, 4, 327-41, 1993.
- Kircher, K.; Kohl, K. D.; Folgueras, M., *Chem. Technik*, 7, 3, 107-10, 1978.
- van Esche, G.; Kromminga T.; Schmidt, A., Soc. Plast. Eng., Inc., Antec, Conf. Proc., 2837, 1998.
- Vincent, O.; Osmont, E., Soc. Plast. Eng., Inc., Antec, Conf. Proc., paper 131, 2002.
- Wypych G., **Polymer Modified Textile Materials**, John Wiley & Sons, New York 1988.
- Wypych G., **Handbook of Fillers**, ChemTec Publishing, Toronto 2000.
- Wypych G., **Handbook of Plasticizers**, ChemTec Publishing, Toronto 2004.
- Coupland, K.; Maltby, A. J.; Parker, D. A., AddCon Asia '97, International Plastics Additives and Modifiers Conference, Singapore, Oct. 28-29, 1997, paper 15, 1-5.
- Janokar A. V.; Hirt, D. E.; Wooster, J. J., Soc. Plast. Eng., Inc., Antec, Conf. Proc., 2887-91, 2002.
- Janokar, A. V.; Hirt, D. E.; Wooster, J. J., *Polym. Eng. Sci.*, 44, 1, 34-44, 2004.
- Muire, L. B.; Hirt, D. E., Soc. Plast. Eng., Inc., Antec, Conf. Proc., 2867-2872, 2000.
- Muire, L. B.; Hirt, D. E., Soc. Plast. Eng., Inc., Antec, Conf. Proc., 3124-27, 1999.
- Wyllin, F., **Plastics Additives Handbook**, Zweifel, H., Ed., Hanser, 2001.
- Sharma, A. H.; Beard, B. C., *J. Vinyl Additive Technol.*, 3, 4, 309-13, 1997.
- Focquet, K., Addcon '95: Worldwide Additives & Polymer Modifiers Conference, Book of

- Papers, Basel, April 5-6, 1995, paper 19, 1-5.
- 22 Owen, M. J. **Encyclopedia of Polymer Science and Engineering**, Release Agents, Mark, H. F., Ed., *John Wiley & Sons*, 1985.
 - 23 Axel, F., *Reinforced Plast.*, **43**, 12, 24-29, 1999.
 - 24 Mori, K.; Sasaki, Y.; Hirahara, H.; Oishi, Y., *J. Appl. Polym. Sci.*, **90**, 2549-56, 2003., 2557-71, 2003.
 - 25 Andrew, S. D.; Swaintek, D. J.; Diem, R.; Nollen, D., Polyurethanes World Congr., Sept. 24-26, 1991, 877-84, 1991.
 - 26 Chen, C. H.; White, J. L.; Ohta, Y., *Intern. Polym. Processing*, **VI**, 3, 212-16, 1991.
 - 27 Meyer, L. W., *J. Cellular Plastics*, **20**, 5, 195-212, 1984.
 - 28 Meyer, L. W., Polyurethane: New Paths Prog., Mark., Technol., Proc. SPI Int. Tech./Mark. Conf., 6th, 370-4, 1983.
 - 29 Briscoe, B. J.; Panesar, S. S., *J. Adhesion Sci. Technol.*, **2**, 4, 287-310, 1988.
 - 30 Keck-Antoine, K.; Lievens, E.; Bayer, J.; Mara, J.; Jung, D-S; Jung, S-L, **Multilayer Flexible Packaging**, *Elsevier*, 2010, pp 37-56.
 - 31 Okada, M.; Yamashita, D; Unno, N; Taniguchi, J, *Microelectronic Eng.*, **123**, 117-20, 2014.

COMPATIBILITY AND PERFORMANCE

Compatibility and solubility are characteristic properties of combinations of two or more materials. The fundamental studies of these properties are very important for solvents and plasticizers, and their results have been discussed in detail in monographic sources.^{1,2}

Properties and performance of inorganic antiblocking additives are not affected by solubility but this is the only exception. Organic antiblocking, release, and slip additives perform in accordance with their solubility in systems into which they were incorporated.

A selection of an additive would be simplified if theoretical prediction is possible and physical data required to make such prediction are available. The actual advancement of research on solvents and plasticizers does not allow us to predict which polymer will be dissolved by which solvent or plasticizer, but it is possible to predict which solvents/plasticizers will not be capable of dissolving a particular polymer. Some results of similar studies are available for additives discussed here and they provide important insight into the behavior of these substances in multi-component systems as well as showing directions for further studies.

Free energy of mixing, ΔG_{mix} , is a known indicator of mutual solubility of materials. It is given by the following equation:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} = V(\delta_1 - \delta_2)^2 \phi_1 \phi_2 - T\Delta S_{\text{mix}} \quad [6.1]$$

where:

ΔH_{mix}	enthalpy of mixing
T	absolute temperature
ΔS_{mix}	entropy of mixing
V	molar volume of mixture
δ_1, δ_2	solubility parameters of the mixture components
ϕ_1, ϕ_2	volume fractions of the mixture components.

If two substances mix together, the free energy of mixing, ΔG_{mix} , is negative, and the more negative it becomes, the better mixing (or mutual solubility) of components is observed. Because absolute temperature and entropy can only be positive, the term $T\Delta S_{\text{mix}}$ is always positive. This means that the best solubility is observed when the enthalpy of mixing equals zero:

$$\Delta H_{\text{mix}} = V(\delta_1 - \delta_2)^2 \phi_1 \phi_2 = 0 \quad [6.2]$$

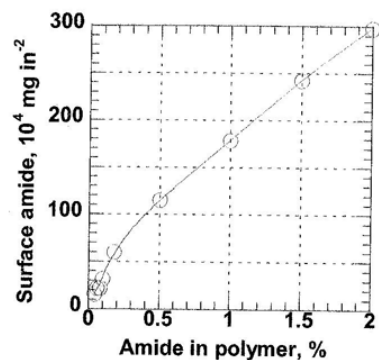


Figure 7.5. The amount of erucamide on the surface of polypropylene film vs. its amount added to polymer. [Data from Schael, G. W., *J. Appl. Polym. Sci.*, **10**, 653-61, 1966.]

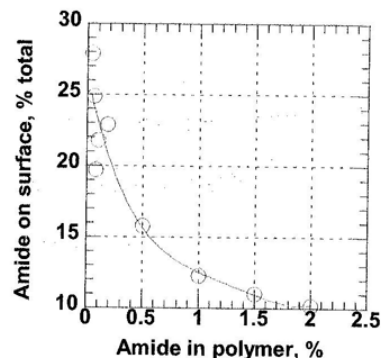


Figure 7.6. The percentage of the total available concentration of erucamide that migrated to the surface of polypropylene film vs. the amount of erucamide added. [Data from Schael, G. W., *J. Appl. Polym. Sci.*, **10**, 653-61, 1966.]

- thickness of the part (thick parts have more additive to diffuse to the same surface)

7.2 DISTRIBUTION OF ADDITIVE IN BULK AND ON SURFACE

Enamel film was cast and baked on the surface of a glass panel. Composition contained 200 ppm of silicone oil. Both surfaces of the film were abraded with potassium bromide powder and composition of the abraded surface was determined by FTIR.¹² Both surfaces were composed of silicone oil but the bulk film did not have any detectable quantity of silicone oil. The top surface (interface with air) contained more oil than the bottom surface (glass).

Oleamide and stearamide were studied by XPS which determined the amount of nitrogen on the surface of polyethylene film. Figure 7.4 shows the percentage of the total surface area of film covered by additive vs. aging time. These data are for 0.1% addition of additive. If the concentration of additive is increased to 0.3%, then oleamide covers the entire surface after 34 days, whereas stearamide covers only 29% of the total surface area after 34 days.¹³ This shows that attainment of full surface coverage depends on the type of additive, time, and the amount added to bulk.

The surface amide concentration depends on the amount of amide added to the material, as seen from the data on polypropylene (Figure 7.5). Figure 7.6 shows that only for the smaller additions of erucamide (0.04 to 0.18%) is its percentage on the surface very high (19.7 to 27.9%), then it drops down to about 10%

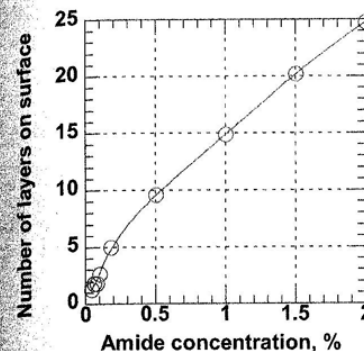


Figure 7.7. Number of monomolecular layers of erucamide on the surface of polypropylene film vs. its concentration in bulk. [Data from Schael, G. W., *J. Appl. Polym. Sci.*, **10**, 653-61, 1966.]

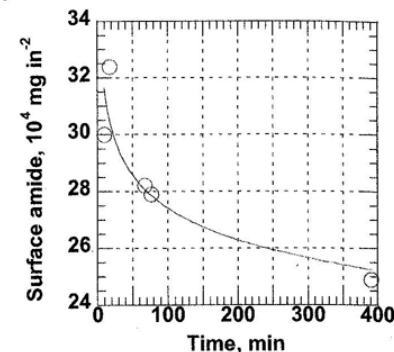


Figure 7.8. Surface coverage of polypropylene film by erucamide vs. time from film manufacture. [Data from Schael, G. W., *J. Appl. Polym. Sci.*, **10**, 653-61, 1966.]

as if the surface has been saturated with erucamide. In industrial practice, erucamide is usually added in concentrations of 0.05 to 0.2%.¹⁴ It should be noted that both sides of a film are covered by additive, therefore the percentages of utilization of erucamide are twice as high as those given in Figure 7.6.

It is interesting to note that for full coverage of the surface, only $12 \times 10^4 \text{ mg in}^{-2}$ of erucamide is needed.¹⁴ This is even met with the smallest addition studied (0.04%). In the practical range of concentrations (0.6 to 0.1%) the number of layers is between 1.81 to 2.66. This is in full agreement with the mechanism outlined in Chapter 5 (see Figure 5.8), which was proposed more than two decades after these data were available.¹⁵

It is interesting to review the data on the effect of time on the surface coverage of polypropylene film. Figure 7.8 shows that the initial concentration of surface amide in a freshly manufactured film is slightly higher and it then drops down. It is understandable, considering that the coefficient of diffusion depends on temperature and causes a higher concentration to be initially available on the surface. Then this excess is apparently reabsorbed. Also, initially there are almost three monomolecular layers on the surface of film which later drop down to two layers. If one looks at the schematic diagrams in Figure 5.8, it is evident that there are thermodynamical reasons for two-layer coverage because two amide groups are at a low energy state when they are oriented towards each other and stabilized in this position by hydrogen bonding. The formation of the third layer is not thermodynamically sponsored because hydrocarbon chains do not have any particular affinity to each other. It can be speculated that the coverage by more than two layers is caused by incompatibility and other reasons (e.g., excessive concentration

or crystallization). In the course of the same study,¹⁴ it was shown that the coefficient of friction of polypropylene film decreases with time, even if there is no additive. This decrease correlates with an increase in polypropylene density, due to its crystallization. It is known (see Figure 5.7) that erucamide resides in the amorphous phase, and if this diminishes due to crystallization, more erucamide will be squeezed out into the surface of the film.

Amide additives which reside on the surface may be degraded by oxidation or UV radiation or lost by evaporation. It was demonstrated that the surface concentration of erucamide did not change with time at room temperature but a drastic decrease in its concentration occurred when temperature was increased to 55°C.¹⁶

Fluoropolymer-based additive reduces rheological parameters of processing by extrusion, which shows that the additive has lubricating action. After processing, no trace of additive was detected on the surface of products.¹⁷ It was concluded that at elevated temperature, additive migrates and resides on the surface of metal parts, which improves processing characteristics.

In sheet molded compounds, mold release agents (stearates of calcium and zinc) were found in the surface layers of molded materials. Their presence influenced the acid/base character of surface layers.^{18,19} In these two research papers,^{18,19} it was pointed out that the surface layer contained no filler but most of the release agent was residing there. Surface accumulation of additives was reported for nitrile butadiene rubber.²⁰ The layers of additives formed are reported to affect adhesion.^{20,21}

7.3 HOW MOBILITY AFFECTS ADDITIVE SELECTION?

Three performance characteristics related to diffusion must be considered:

- ability to form surface layers, which reduces blocking and coefficient of friction and the time-scale of the diffusion process. This is important for antiblocking and slip functions. Here efficient migration to the surface and fast replenishment of additive lost (degradation, evaporation contact with rollers, etc.) are the key performance characteristics during production, processing, and use
- ability to separate two materials to reduce their adherence. This is an important function for release agents. In this case, additive should not migrate from the mold surface into the material bulk during processing. In some cases it will be advantageous for additive to be reabsorbed from the surface into the material bulk or to be left on the mold surface or process equipment surface
- post production operations. This is important for all three types of additives. Some additives may interfere with product quality by affecting adhesion, color, clarity, etc.

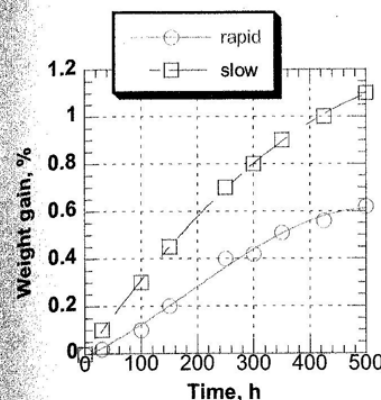


Figure 7.9. Diffusion of erucamide to LLDPE films cooled slowly and rapidly vs. time. [Data from Joshi, N. B.; Sakhalakar S. S; Hirt D. E., Soc. Plast. Eng., Inc., Antec, Conf. Proc., 2406-10, 1996.]

reduces their presence on a formed part. It is difficult to find additives which perform in this manner. Diffusion coefficient is reduced with temperature decreasing, which slows down the rate of additive movement when a part is formed. In order to accelerate additive migration from the surface to material bulk, a mechanism is required which reduces the additive concentration in the material bulk to create a concentration gradient which promotes such migration. These types of mechanisms require complex properties which are not a common part of additive design.

7.4 ADDITIVE TRANSFER TO MATERIAL IN CONTACT

Linear low density polyethylene, LLDPE, films were molded and cooled slowly and rapidly.²² The films were then contacted with solid erucamide for different periods of time at room and elevated temperatures. Figure 7.9 shows that slowly cooled film gains weight more rapidly than fast cooled LLDPE film. Slow cooling produces film having higher crystallinity and higher free volume. High free volume increases the diffusion rate, especially when bulky molecules are involved.

There are publications on films composed of several layers of the same or different polymers.^{7,23-26} These studies give some preliminary data on diffusion to materials in contact. The data cannot be interpreted yet to form a consistent description of phenomena. Below, some observations are listed:

- two-layer film was made out of LLDPE by coextrusion, using erucamide-free granulate for one layer and granulate containing 1% erucamide for another layer. Erucamide profiling in both layers shows that concentra-

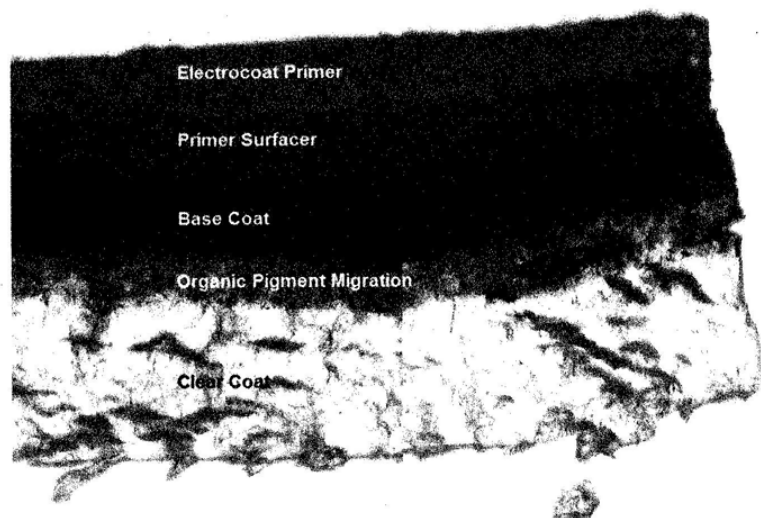


Figure 7.13. Optical micrograph of an automotive paint cross-section obtained from a red Mazda. [Adapted, by permission, from Maric, M.; van Bronswijk, W.; Lewis, S. W.; Pitts, K.; Martin, D. E., *Forensic Sci. Int.*, **228**, 165-169, 2013.]

Figure 7.13 shows that additives can migrate not only to the surface with air but they also migrate into adjacent layers as in the case of red pigment migrating from the basecoat into clearcoat. This is true for all lower molecular weight additives.³¹ High molecular weight substances do not readily migrate between layers.³¹

REFERENCES

- 1 Quijada-Garrido, I.; de Velasco-Ruiz, M. F.; Barrales-Rienda, J. M.; *Macromol. Chem. Phys.*, **201**, 3, 375-81, 2000.
- 2 Pace, R. J.; Dadyner, A., *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 437, 1979.
- 3 Pace, R. J.; Dadyner, A., *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 453, 1979.
- 4 Pace, R. J.; Dadyner, A., *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 465, 1979.
- 5 Pace, R. J.; Dadyner, A., *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 1103, 1979.
- 6 Pace, R. J.; Dadyner, A., *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 1169, 1979.
- 7 Gagliardi, C. A.; Muire, L. B.; Hirt, D. E., Soc. Plast. Eng., Inc., Antec, Conf. Proc., 2502-2506, 1999.
- 8 Joshi, N. B.; Hirt D. E., Soc. Plast. Eng., Inc., Antec, Conf. Proc., 2832-2836, 1998.
- 9 Botros, M. G., Annual Technical Conference - Society of Plastics Engineers, 3653-59, 1995.
- 10 Botros, M. G., *J. Plast. Film Sheeting*, **11**, 4, 326-37, 1995.
- 11 Kefaleas, C.; Billingham, N. C., *Polym. Preprints*, **42**, 1, 350-1, 2001.
- 12 Johnson, W. T. M., *Official Digest, Federation of Societies for Paint Technology*, **33**, 1489-1502, 1961.
- 13 Sharma, A. H.; Beard, B. C., *J. Vinyl Additive Technol.*, **3**, 4, 309-13, 1997.
- 14 Schael, G. W., *J. Appl. Polym. Sci.*, **10**, 653-61, 1966.
- 15 Coupland, K.; Maltby, A. J.; Parker, D. A., AddCon Asia '97, International Plastics Additives and Modifiers Conference, Singapore, Oct. 28-29, 1997, paper 15, 1-5.

- 16 Shuler, C. A.; Janokar A. V.; Hirt, D. E., Soc. Plast. Eng., Inc., Antec, Conf. Proc., 2724-28, 2003.
- 17 Focquet, K., Addcon '95: Worldwide Additives & Polymer Modifiers Conference, Book of Papers, Basel, April 5-6, 1995, paper 19, 1-5.
- 18 Vallat, M.-F.; Schultz, J.; Mauzac, C.; Jacquip, M., *Polym. Adv. Technol.*, **10**, 4, 237-243, 1999.
- 19 Serre, C.; Vayer, M.; Erre, R.; Ollive, C., *J. Mater. Sci.*, **34**, 17, 4203-08, 1999.
- 20 Rawls A. S.; Joshi, N. B.; Sakhalkar S. S.; Hirt D. E., Soc. Plast. Eng., Inc., Antec, Conf. Proc., 3029-35, 1997.
- 21 Brydson J., *Plastic Materials*, Elsevier 1999.
- 22 Joshi, N. B.; Sakhalkar S. S.; Hirt D. E., Soc. Plast. Eng., Inc., Antec, Conf. Proc., 2406-10, 1996.
- 23 Sankhe, S. Y.; Hirt, D. E., Soc. Plast. Eng., Inc., Antec, Conf. Proc., 2877-2881, 2002.
- 24 Sankhe, S. Y.; Hirt, D. E.; Roberts, W. P.; Havens, M. R., Soc. Plast. Eng., Inc., Antec, Conf. Proc., 2516-2520, 1999.
- 25 Schumann, B. H.; Wooster J. J., Soc. Plast. Eng., Inc., Antec, Conf. Proc., paper 1081, 1999.
- 26 Bryant, K. A. A., Polym., Laminations Coat. Conf., San Francisco, Aug. 30-Sept. 3, 1998, 969-77, 1998.
- 27 Joshi, N. B.; Hirt, D. E., *Appl. Spectroscopy*, **53**, 1, 11-16, 1999.
- 28 Shuler, C. A.; Janokar A. V.; Hirt, D. E., Soc. Plast. Eng., Inc., Antec, Conf. Proc., 2724-28, 2003.
- 29 Ramirez, M. X.; Hirt, D. E.; Miranda, N., Soc. Plast. Eng., Inc., Antec, Conf. Proc., 2654-2657, 2001.
- 30 Chen, J.; Li, J.; Hu, T.; Walther, B., *J. Vac. Sci. Technol.*, **25**, 4, 886-92, 2007.
- 31 Dragnevski, K. I.; Donald, A. M.; Clarke, S. M.; Maltby, A., *Colloids Surfaces A: Physicochem. Eng. Aspects*, **337**, 47-51, 2009.
- 32 Maric, M.; van Bronswijk, W.; Lewis, S. W.; Pitts, K.; Martin, D. E., *Forensic Sci. Int.*, **228**, 165-169, 2013.