

The Expansion of Sumilizer G Series –The Excellent Additives for Polymer–

Sumitomo Chemical Co., Ltd.
Fine Chemicals Research Laboratory
Fumitoshi KOJIMA

Sumilizer G series are the excellent additives for maintaining the function of a polymer material. They consist of Sumilizer GM, Sumilizer GS, Sumilizer GA-80 and Sumilizer GP. They are developed as the fruits of evaluation and synthetic technologies of Sumitomo Chemical. We have been studying on their new applications through not only the evaluation of performance but also the confirmation of hypothetical working mechanism. In this review, the outlines of unique functions of Sumilizer G series and the expanded new applications are shown.

This paper is translated from R&D Report, “SUMITOMO KAGAKU”, vol. 2004-I.

Introduction

Macromolecular materials, such as plastics, consist of polymer components that provide primary functionality, as well as a variety of additives that provide supplemental functionality. As indicated in **Table 1**, there are a variety of different types of additives for polymers. Additives can be roughly classified into two types: those utilized to maintain the existing functionality of macromolecular materials and those used to provide additional functionality to macromolecular materials. Polymer materials are supplied to the market for use as final products only after they have completed the

entire manufacturing process, from the creation of the polymer itself, the blending in of a variety of additives, molding and assembly. Thus, during each manufacturing process, macromolecular materials are exposed to stresses, such as heat, mechanical shear forces that decrease molecular weight or generate gelation caused by crosslinking. Moreover, during usage, macromolecular materials are also exposed to a variety of environmental stresses, such as heat, light and gas that affect them by oxidation and discoloration. For this reason, additives to maintain the existing functionality of macromolecular materials (also referred to as stabilizers) are incorporated into almost all macromolecular materials. Meanwhile, the additives used to provide additional functionality to a polymer material are blended in only when needed.

Currently, the Sumilizer® G Series includes 4 types of products: Sumilizer GM, Sumilizer GS, Sumilizer GA-80 and Sumilizer GP. All of these products are additives that are used to maintain the existing functionality of macromolecular materials. These 4 products possess outstanding performance. They were developed as the fruit of our company’s synthesis and evaluation technologies. During the development of the Sumilizer G Series, we not only evaluated the performances, but also studied the manner in which their unique properties were manifested. In addition, we were able to clarify their working reaction mecha-

Table 1 Examples of Additives for polymer

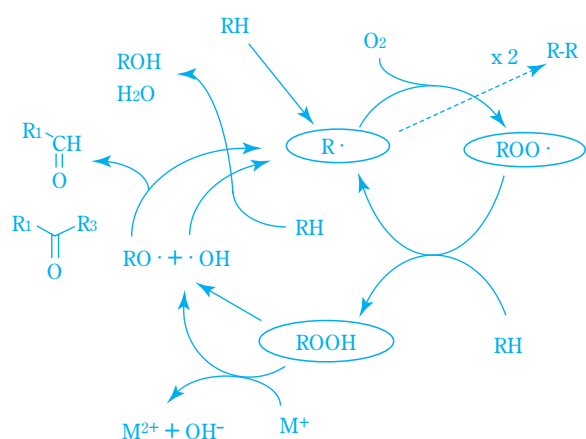
	Function	
	Preservation	Addition
Plasticizers	✓	✓
Antioxidants	✓	
Light stabilizers	✓	
Antibacterials	✓	✓
Lubricants		✓
Impact modifiers		✓
Foaming agents		✓
Crosslinking agents		✓
Nucleating agents		✓
Antistats		✓
Flame retardants		✓
Fillers		✓
Pigments		✓

nisms.¹⁾⁻⁷⁾ Furthermore, based on the study of these reaction mechanisms, we have been able to expand the range of applications for our products. Some of the results from these studies have already been introduced in this publication.⁸⁾ In this paper, we now introduce the structure of our Sumilizer G Series products and explain several new applications that have materialized during the course of their development.

Structure of the G Series

Basically, the structures of the Sumilizer G Series have been designed to respond to the degradation mechanisms that affect polymers. First of all, polymer degradation is explained below.

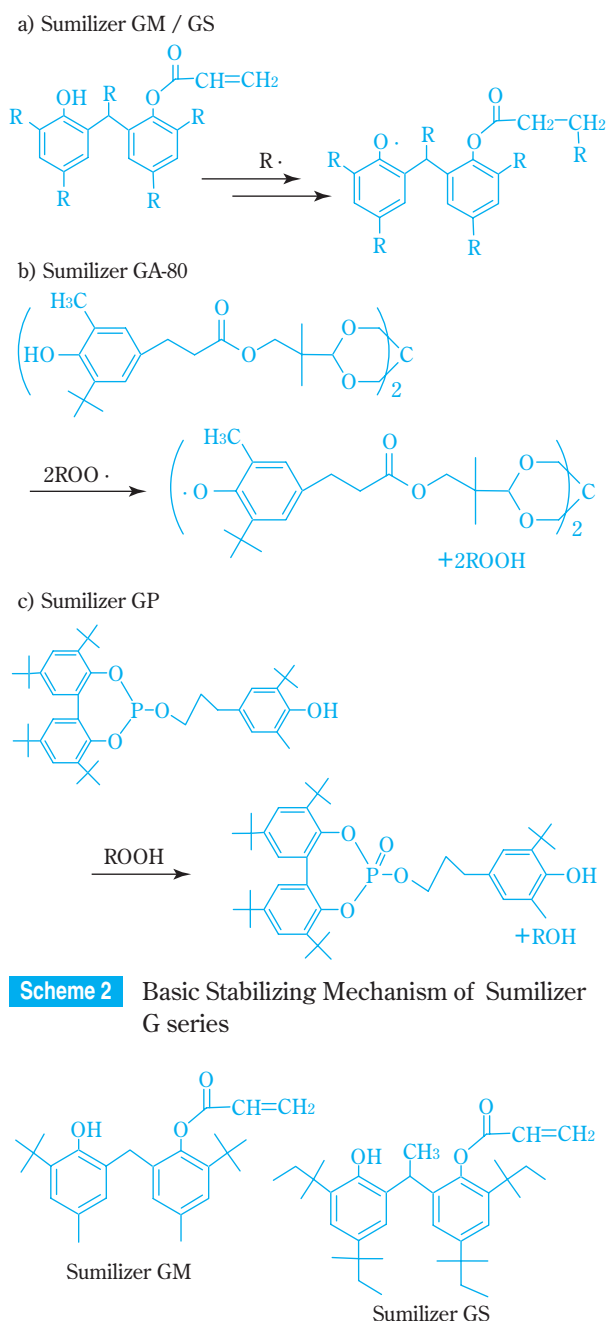
Scheme 1 depicts an overview of the mechanism behind the heat degradation of polymers. Polymer (RH) produces a carbon radical ($R\cdot$) when exposed to environmental stresses, such as heat or light. In the event that the life of the $R\cdot$ is relatively long, a crosslinking reaction will occur due to the coupling of the $R\cdot$ with another $R\cdot$. On the other hand, in the presence of air, the $R\cdot$ derived from the polymer will react with oxygen and becomes a peroxy radical ($ROO\cdot$). The newly-generated $ROO\cdot$ will then attract an $H\cdot$ from the surrounding RH, reacting to form a hydroperoxide (ROOH) and simultaneously generating another $R\cdot$. These processes continue repeatedly, resulting in the progressive oxidation degradation of the polymer. Furthermore, ROOH is unstable and its decomposition produces new radicals (such as $RO\cdot$). As these new radicals extract more $H\cdot$ from RH and increase the number of $R\cdot$, the oxidative degra-



Scheme 1 Degradation mechanism of polymer by heat

ation of the polymer begins to accelerate. Therefore, even though oxidative degradation begins slowly, the speed of degradation later increases due to the generation of ROOH. This process is referred to as auto-oxidation. In this degradation mechanism, each of the 3 elements: $R\cdot$, $ROO\cdot$ and ROOH, plays an important role. However, the particular type of polymer and the exposure conditions will determine which of these 3 degradation mechanisms will contribute the most predominant role.

Scheme 2 depicts the basic stabilizing mechanisms behind each of the Sumilizer G Series products, which have been designed to protect polymers against degradation mechanisms. As shown in **a)**



of Scheme 2, both Sumilizer GM and Sumilizer GS act by stabilizing¹⁾ the R· by bonding to the R· at the acrylate group, thus converting it into a more stable phenoxy radical. Sumilizer GA-80 stabilizes ROOH, as shown in **b)** of Scheme 2, through the following actions: it provides an H· to ROO·, allowing it to become ROOH, then Sumilizer GA-80 is itself converted into a stable phenoxy radical. Sumilizer GP provides stabilization for ROOH by guiding the ROOH to a stable ROH, as is shown in **c)** of Scheme 2. Thus, Sumilizer G Series products work together to provide stabilization against all 3 major polymer degradation elements. Even though there exists some duplication of functionality between Sumilizer GS and Sumilizer GM, Sumilizer GS is an upgraded version of Sumilizer GM and provides better stabilization of R· and greater resistance to discoloration than does Sumilizer GM⁴⁾⁻⁶⁾.

Sumilizer® GM/GS

As described above, both Sumilizer GM and Sumilizer GS can stabilize R·. However, R· stabilization is only required in a rather limited number of situations. Macromolecular materials are usually processed in the presence of air, therefore the R· produced during polymer degradation reacts with the oxygen in the air, eventually causing oxidative degradation. However, when using polymers that have relatively long R· lifespans, such as butadiene type polymers, a crosslinking reaction occurs due to coupling between an R· and another R·, during processes with presence of minimal shared oxygen in the surrounding environment. This crosslinking reaction causes undesired polymer gelation. Sumilizer GM is the first polymer additive in the world to possess an R· stabilization function. Prior to our development of Sumilizer GM, the need to stabilize R· had never been recognized.

Fig. 1 depicts an example of Sumilizer GM performance in styrene butadiene rubber (referred to as SBR hereafter). During the processing of macromolecular materials, the polymer is subjected to heat and shear forces, resulting in polymer degradation, as previously described. Using a Lab-plastomill to aid in evaluations, a quantitative measure of process stabilization performance can be readily obtained from the changes in the torque value for the polymer. During the processing of SBR,

the torque value temporarily rises as processing progresses, due to the breakage of molecular chains, crosslinking and perhaps even decomposition that may occur with degradation. After reaching a peak, the torque value then decreases. The longer the amount of time required to reach the torque peak, the slower is the progression of degradation. Therefore, it is apparent that a polymer additive that can extend the time required to reach the torque peak will exhibit better process stabilization performance. In Fig. 1, the vertical axis represents the amount of time required to reach the torque peak (Gel build-up time) and the horizontal axis represents the quantity of polymer additive. While **AO-1**, an additive that had been utilized before the development of Sumilizer GM, did not improve the performance even at greater loading levels, Sumilizer GM resulted in significantly improved performance at comparable loading levels.

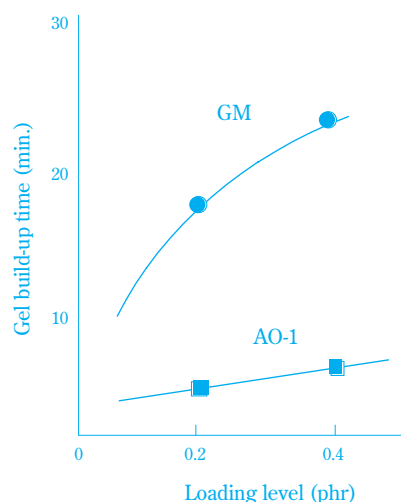
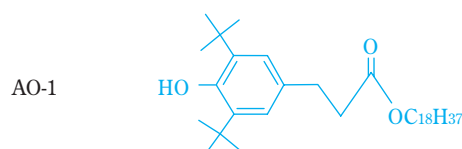


Fig. 1 Performance of Sumilizer GM polymer ; SBR processing condition ; under N₂, at 180°C



Thus, commercial utilization of Sumilizer GM was initiated subsequent to its discovery as a unique performance enhancer for butadiene type polymers, including SBR and styrene butadiene styrene block copolymer (referred to as SBS hereafter). We have also discovered that Sumilizer

GM has performance enhancing effects on styrene isoprene styrene block copolymer (referred to as SIS hereafter).⁹⁾ At the same time, we continued our studies in order to take advantage of the first known polymer R· stabilization function in the world for polymer application. Furthermore, we discovered that both Sumilizer GM and Sumilizer GS demonstrate unique performance during high temperature polymer processing, even when used in olefin polymers having an R· lifespan that is shorter than that of butadiene type polymers.

Fig. 2 depicts a condition in which the ratio of the abundance of R· and ROO· becomes 1:1, under the assumption that the equilibrium relationship specified by **equation 1** is present.¹⁰⁾ (In reality, this equilibrium relationship does not exist, as the ROOH generated will decompose.) Fig. 2 suggests that for polymers having a relatively short R· lifespan, the degradation caused by R· cannot always be ignored, depending upon the conditions. Taking into account this fact and the working mechanisms of Sumilizer GM and GS, the possibility exists that they may provide stabilization for polyolefins. **Fig. 3** shows the results of a study conducted on polypropylene (referred to as PP hereafter) based on the above hypothesis. The vertical axis represents the polymer melt flow rate and the horizontal axis represents the frequency of PP exposure to the molding conditions. If PP is repeatedly exposed to the molding conditions, molecular breakage will occur, resulting in an undesired increase in the polymer melt flow rate. The following two types of antioxidants are most com-

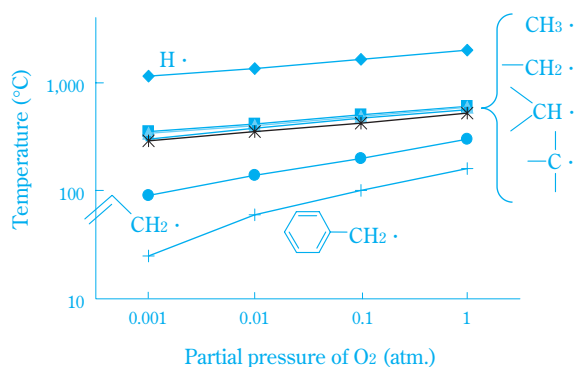


Fig. 2 Approximate Ceiling Temperature for the Gas Phase Equilibrium (1) at Different Partial Pressures of O₂



monly utilized to stabilize PP under the molding conditions: a phenolic antioxidant that provides effective stabilization for ROO· (i.e., **AO-2**) and a phosphorus antioxidant (i.e., **P-1**) that provides effective stabilization for ROOH. Under the standard molding conditions shown in **a)** of Fig. 3, adequate processing stabilization is achieved through using either AO-2 or P-1. The special characteristics provided by Sumilizer GS are not apparent. However, under the harsh molding conditions shown in **b)** of Fig.3, Sumilizer GS demonstrates far greater stabilizing effects than that shown by either AO-2 or P-1. **Fig. 4** depicts the

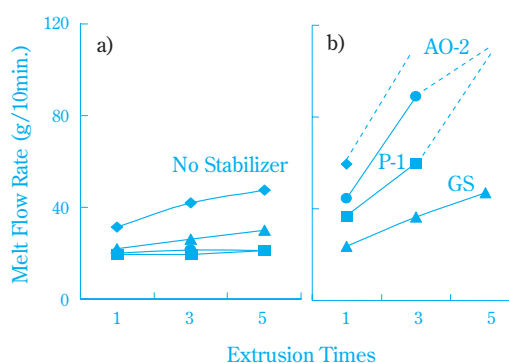


Fig. 3 Processing stability of Polypropylene
Extrusion temp. a) : 190°C, b) : 270°C

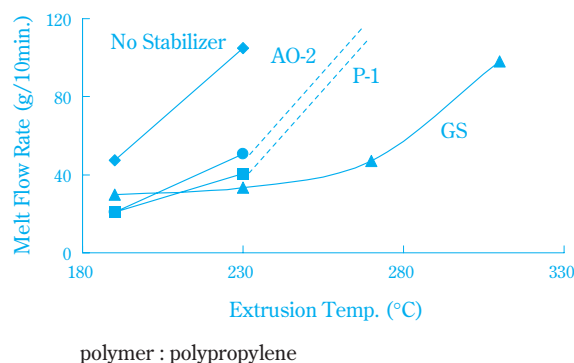
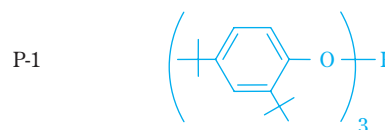
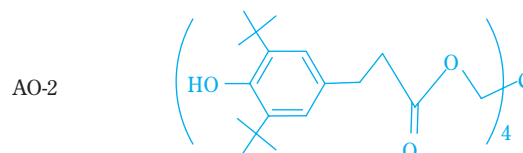


Fig. 4 Dependence of processing stability on extrusion temperature
polymer : polypropylene

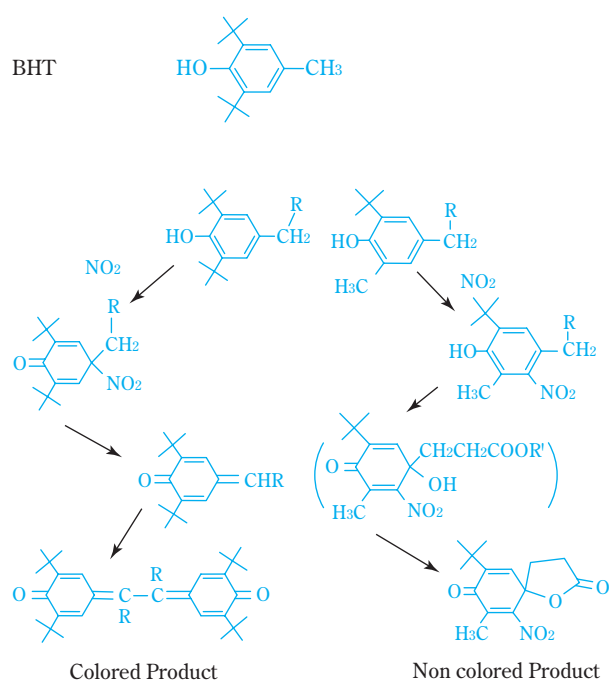
temperature dependence of stabilizing performance. The vertical axis represents the changes in the melt flow rate and the horizontal axis represents the extrusion temperature. As the extrusion temperature increases (meaning that molding conditions are becoming more harsh), the unique stabilizing effect of Sumilizer GS becomes apparent.

Since Sumilizer GS is effective in stabilizing polyolefins at high processing temperatures, it has already been employed in commercial usage. We now expect that Sumilizer GS will find further use as an additive that contributes to expanding the range of applications for polyolefins.

Sumilizer® GA-80

Sumilizer GA-80 is an additive that was developed in order to address certain deficiencies in AO-2, a general-purpose phenolic antioxidant. Although AO-2 has been utilized in a variety of polymers, it was utilized most often in PP, with respect to both the quantity of polymer produced and the amount of stabilizer required. Sumilizer GA-80 possesses a remarkably effective ability to stabilize $\text{ROO}\cdot$. It was developed primarily to target PP applications and has already been put into commercial usage.

Sumilizer GA-80 also possesses another excellent characteristic, which is its outstanding resistance to discoloration. **BHT**, the most basic phenolic antioxidant, has the following two major problems: poor resistance to vaporization due to its low molecular weight; poor resistance to and discoloration due to the fact that it becomes colored¹⁾ due to reactivity with NO_x , thus discoloring the polymer material itself. AO-2 is an antioxidant that was created by improving the vaporization resistance of BHT by increasing its molecular weight. However, the problem with BHT's poor resistance to discoloration has not yet been resolved for AO-2. For both BHT and AO-2, both of o-positions to the phenolic OH are occupied by the t-butyl moiety. However, in Sumilizer GA-80, one of the o-position to phenolic OH is occupied by a methyl moiety. From our investigation into this structural difference, we have discovered that Sumilizer GA-80 possesses a different NO_x reactivity than does BHT. In addition, Sumilizer GA-80 does not easily become colored due to reactivity with NO_x (**Scheme 3**).³⁾ From this information, we have also focused upon develop-



Scheme 3 Reaction pathway of phenolics with NO_x

ing Sumilizer GA-80 for use in applications within areas that require both the resistance to discoloration and the stabilization of $\text{ROO}\cdot$. As a result, Sumilizer GA-80 is now available for use in polyethylene, polyamide and polyacetal.

We intend to expand the utility of Sumilizer GA-80 in order to take advantage of its outstanding resistance to discoloration. We have focused primarily upon the development of applications in polyurethanes, in addition to usage in resins, such as PP. A variety of polyurethanes can be synthesized, including thermoplastic, coating materials and adhesives, due to the choice of its isocyanate and polyol components. Of these two components, isocyanate and polyol, isocyanates usually incorporate aromatic chemical compounds. However, the aromatic ring contained within the molecular chain of a polyurethane reacts with NO_x and the polyurethane itself produces coloration. Although non-aromatic isocyanates can be utilized to prevent this discoloration, they may cause loss of the polymer's properties. Since polyurethane elastic fibers are often utilized in the creation of clothing, while the possession of an aromatic ring is mandatory with respect to the physical properties required, the resistance to discoloration is also important in actual product applications.

AO-3 has been utilized as a stabilizer in polyurethane elastic fibers, ever since the fibers

were developed. As with Sumilizer GA-80, the methyl moiety occupies one of the o-positions on the phenolic OH of AO-3. Therefore, we also initiated investigations into several of its other properties, in addition to its resistance to NO_x-induced discoloration. As an example of the results, **Fig. 5** depicts the resistance of polymer material to discoloration when exposed to light. The vertical axis represents the Yellowness Index for the polymer material. The higher the numeric value, the greater the yellowness. The horizontal axis represents the amount of light exposure. The higher the numeric value, the greater the amount of light exposure. This graph indicates that Sumilizer GA-80 possesses greater resistance to the discoloration

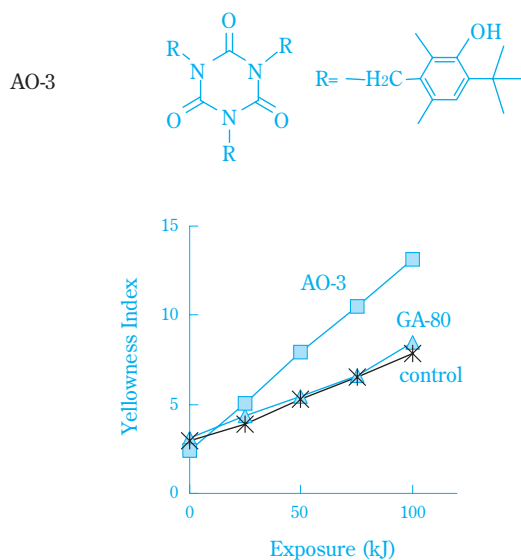


Fig. 5 Discoloration against Light

Exposure condition : Xenon arc, B.P.T. ; 63°C, without spray
 polymer : Thermoplastic polyurethane (polyether type)
 Sample : Injection sheet [t=1mm]

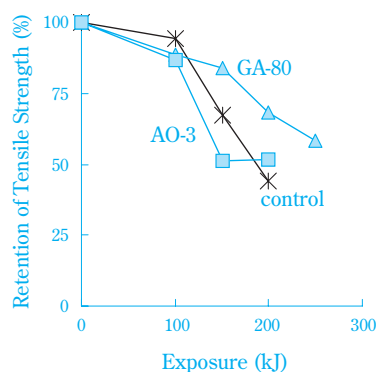


Fig. 6 Mechanical Property against Light

Exposure condition : Xenon arc, B.P.T. ; 63°C, without spray
 polymer : Thermoplastic polyurethane (polyether type)
 Sample : Press sheet [t=0.1mm]

induced by light exposure than does AO-3. From Fig. 5, it can be assumed that the AO-3 itself becomes colored, as the degree of yellowing is stronger in the presence of the AO-3, than in its absence. **Fig. 6** depicts changes in the mechanical strength of the polymer material, when exposed to light. The vertical axis represents the tensile strength after exposure, with the tensile strength prior to exposure being defined as 100. The horizontal axis represents the amount of light exposure. This graph indicates that Sumilizer GA-80 retains a greater amount of its strength when a phenolic antioxidant is present, than when it is not present. With respect to degradation due to light exposure, although R· is produced and auto-oxidation starts, it is apparent that Sumilizer GA-80 continues to provide some stabilizing functionality.

Sumilizer GA-80 has already been commercialized for usage in polyurethane elastic fiber. The amount of polyurethane elastic fiber produced has been increasing rapidly in recent years, therefore we are continuing to enhance Sumilizer GA-80 and are aiming to expand its range of applications.

Sumilizer® GP

Sumilizer GP is the first hybrid-type phosphorus antioxidant in the world. The only type of phosphorus antioxidants created so far possess a structure in which a trivalent phosphorus atom (a functional group providing ROOH stabilization) is incorporated within each molecule (refer to Scheme 2). Sumilizer GP is designed to have the phenolic moiety, which possesses the ROO· stabilization function, to be located in a specific position on the molecule. Thus, the utilization of these two functional groups, the trivalent phosphorus atom and the phenolic moiety,⁷⁾ allows Sumilizer GP to achieve the improved stabilizing performance that is demanded from a phosphorus antioxidant, under molding conditions.

Sumilizer GP has been developed particularly for use with linear low density polyethylene (referred to as LLDPE hereafter). Most LLDPE is used in the manufacture of polymer film. One typical defect during film processing is the generation of “fish-eye”. Fish-eye resemble the “eye of a fish” and mar the surface appearance of the smooth film. **Fig. 7** depicts the performance of Sumilizer GP in

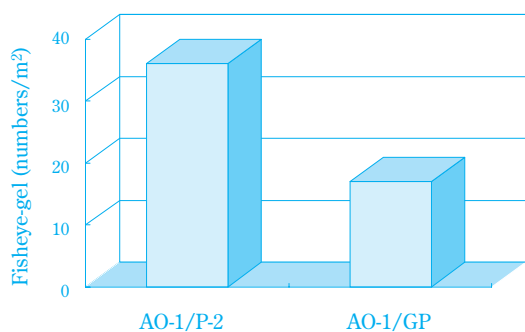


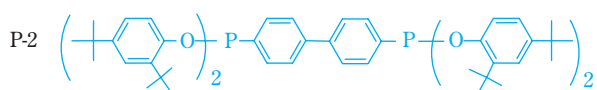
Fig. 7 Performance of Sumilizer GP

Polymer : LLDPE, Inflation film (45 μ m)

Test condition :

Processing temp. ; 220°C

Sampling : for 1hr (40m)



LLDPE. The vertical axis represents the frequency of fisheye occurrence. The lower the numeric value, the better the performance. The use of Sumilizer GP significantly reduces the frequency of fisheye occurrence as compared to **P-2**, which is used as a general-purpose additive. Sumilizer GP also possesses other outstanding functionality, such as excellent resistance to discoloration and hydrolysis. For this reason, we are currently focusing upon expanding the range of Sumilizer GP applications in the area of LLDPE, thus rapidly growing its commercial market utilization.

In addition to its original function of stabilization during processing, Sumilizer GP possesses outstanding resistance to discoloration, which is also a characteristic of Sumilizer GA-80. We are currently examining PP applications for Sumilizer GP, particularly in the area of PP fiber. For usage in PP fiber, a high degree of process stabilization is required, as PP fiber production utilizes the melt spinning process. A high degree of resistance to discoloration is also required, as PP finished products are made in the form of threads, which possess a large specific surface area.

Fig. 8 indicates the results of a study performed using Sumilizer GP in PP. The vertical axis represents the difference in the melt flow rate (Δ MFR) after repeated extrusions (repeated 5 times in this test). In the graph, since molecular breakage occurs due to degradation, a lower numeric value

indicates better performance. The horizontal axis represents changes in the yellowing index (Δ YI) of PP sheets containing different types of additives, after exposure to NO_x. On this axis, the lower the numeric value, the better the performance. The graph shows that Sumilizer GP formula (GP/P-1) performs better than general-purpose **AO-4**/P-1 and **AO-5**/P-1. Moreover, as compared to **H-1**/**M-1**, which is used for special purposes, the Sumilizer GP formula also demonstrates better performance. PP fibers are utilized far more in the US and Europe than in Japan, due to differences in lifestyles. From the data in this study, we have already begun to introduce Sumilizer GP to manufacturers within

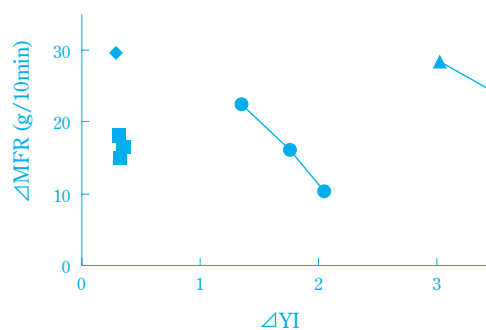


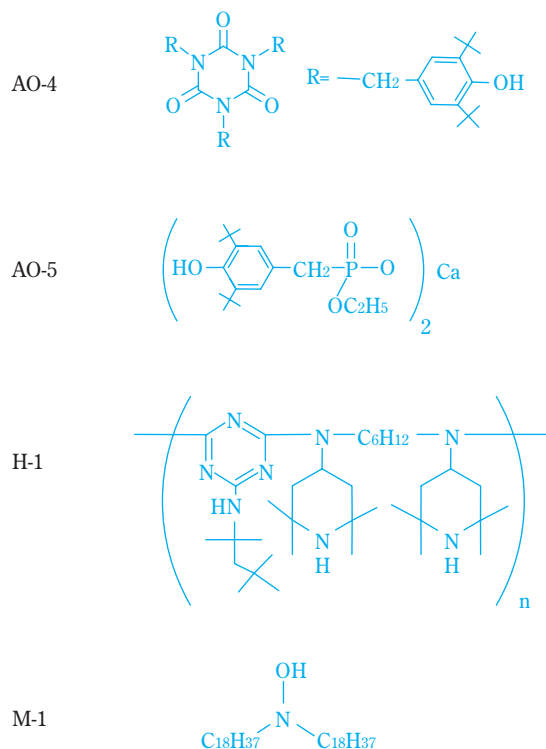
Fig. 8 Performance of Sumilizer GP on PP fiber

Processing condition : temp ; 250°C, extruded for 5 times

NO_x gas exposure condition : 1%NO_x for 1hr

Formulation : ■ ; GP/P-1, ● ; AO-4/P-1,

▲ ; AO-5/P-1, ◆ ; H-1/M-1



the US and Europe.¹²⁾ We are planning to conduct even more detailed evaluations to determine additional applications for Sumilizer GP in the area of PP fiber.

Conclusion

In this paper, I have introduced the structure of the Sumilizer G Series and have presented special features and applications for each individual product. All of the Sumilizer G Series products possess unique secondary characteristics, in addition to the basic functionality indicated in Scheme 2. We are planning to develop new applications for our Sumilizer G Series products by making the most of their unique properties, without limiting their current range of use. For the future expansion of Sumilizer G Series products, the comprehensive support capabilities provided by our company will become even more important. These comprehensive support capabilities shall include not only the development of new applications, but also the processes involved with product manufacture and sale. We shall focus our market development efforts into an integrated system that combines together all of the important aspects of product research, manufacturing and sales.

Furthermore, during the development of Sumilizer GP, we have also developed stabilizers that can protect against each of the 3 elements causing degradation: R·, ROO· and ROOH, each of which contributes to polymer degradation. However, in the course of developing new applications for each Sumilizer G Series product, it has become apparent that our existing Sumilizer G Series products alone are not capable of completely eliminating all polymer degradation problems. Therefore,

we shall continue to develop new generations of Sumilizer G Series products, in order to respond to this new challenge.

Reference

- 1) S. Yachigo, M. Sasaki, Y. Takahashi, F. Kojima, T. Takada, T. Okita : Polym. Degrad. Stab., 22, 63-77 (1988)
- 2) S. Yachigo, M. Sasaki, F. Kojima, : Polym. Degrad. Stab., 35, 105-113 (1992)
- 3) S. Yachigo, M. Sasaki, T. Ishii, S. Tanaka, K. Inoue : Polym. Degrad. Stab., 37, 99-106 (1992)
- 4) S. Yachigo, F. Kojima, M. Sasaki, K. Ida, S. Tanaka, K. Inoue : Polym. Degrad. Stab., 37, 107-113 (1992)
- 5) S. Yachigo, K. Ida, M. Sasaki, K. Inoue, S. Tanaka : Polym. Degrad. Stab., 39, 317-328 (1993)
- 6) S. Yachigo, M. Sasaki, K. Ida, K. Inoue, S. Tanaka, Y. Honda, E. Fukuyo, K. Yanagi : Polym. Degrad. Stab., 39, 329-343 (1993)
- 7) K. Fukuda, K. Miyake : 2001 SPSJ Symposium on Degradation and Stabilization of Polymer (2001)
- 8) Sumitomo Kagaku 1985-II 42-55 (1985)
Sumitomo Kagaku 1987-II 14-28 (1987)
Sumitomo Kagaku 1994-I 14-22 (1994)
Sumitomo Kagaku 2002-II 42-49 (2002)
- 9) K. Miyake, K. Fukuda, M. Sasaki : proceedings of the 1998 TAPPI Hot Melt Symposium 221-229 (1998)
- 10) S.W.Benson : J. Amer. Chem. Soc., 87, 972-979 (1965)
- 11) K. C. Smeltz : Textile Chem. Color., 15(4), 52-56 (1983)
- 12) K. Kimura, F. Kojima, K. Fukuda : SPE Polyolefins 2004 Conference Section IX

PROFILE



Fumitoshi KOJIMA

Sumitomo Chemical Co., Ltd.
Fine Chemicals Research Laboratory
Senior Research Associate