New Development of Polymer Additives

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In response to specific customer needs, we have developed SUMILIZER® GP, SUMILIZER® GS, SUMILIZER® GM, SUMILIZER® GA-80 polymer additives (stabilizing agents) as unique products which have properties hitherto unseen. We have utilized these new properties to apply these unique products in a wide range of applications. This paper describes the mechanism of polyolefin stabilizing agents, and also trends in customer needs as a result of changes in the market environment, and presents the responses our company has made in the field of additives due to these factors. We will also introduce some of the steps we have been taking toward development of our new G series.

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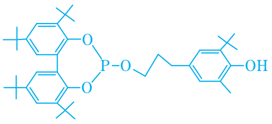
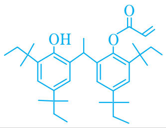
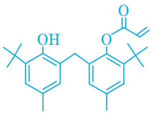
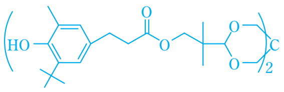
Introduction

We of Sumitomo Chemical Co., Ltd., have launched SUMILIZER® GP, SUMILIZER® GS, SUMILIZER® GM and SUMILIZER® GA-80 (hereinafter referred to as GP, GS, GM and GA-80 respectively; all of which are collectively referred to as the “G series”) as new polymeric additive products (stabilizing agents) designed to meet the various needs of our customers (**Table 1**). Accordingly, these new products boast properties not heretofore seen in any previous formulation. Making the most of these unique properties, we are striving to expand the applications of the products (**Table 1**).

This paper describes the deterioration mechanism, stabilization mechanism, process stability and stabilization mechanism of polyolefin. Additionally, it outlines changes in customer needs with regard to polyolefin products due to changes in the market environment, and it presents our means of response to these changes through the development of new additives. Moreover, it introduces some of the steps undertaken by our company for the development of the new G series.

Table 1 Our original development product

Product	Chemical Structure	Main Application
SUMILIZER® GP		LLDPE, HDPE, LDPE, PP
SUMILIZER® GS		SBS, ABS, PS, PP, HDPE
SUMILIZER® GM		SBS, SBR, ABS, BR
SUMILIZER® GA-80		HDPE, PP, PU

Deterioration Mechanism of Polyolefin

Scheme 1 outlines a polymer’s thermal deterioration mechanism and stabilization mechanism using a phenolic antioxidant (Ar-OH) and a phosphorus-based antioxidant.

Polyolefin (RH) produces alkyl radical (R•) due to the effects of heat and mechanical shearing force.

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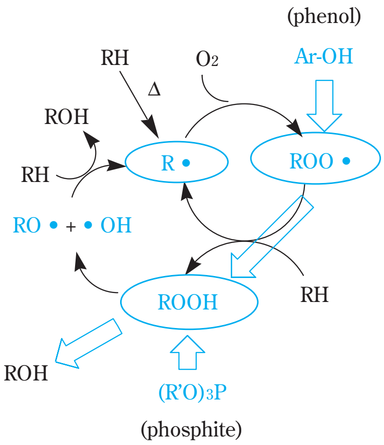


Scheme 1 Auto-oxidation mechanism of polyolefins

Furthermore, under the coexistence of oxygen, R• reacts to the oxygen and produces peroxyl radical (ROO•). The ROO• produced by polyolefin extracts hydrogen from RH and reproduces R•, whereby the ROO• turns to hydroperoxide (ROOH).

The polymer deterioration progresses through repetition of the above cycle. Additionally, ROOH, which is unstable, produces new radicals (such as RO•) while it's decomposing. These new radicals extract H• from RH and increase R•, thereby accelerating the oxidation degradation of the polymer. Consequently, although the deterioration has been slow initially, it advances like a chain reaction through the production of ROOH. Thus it is referred to as auto-oxidation of polyolefin.[1)] However, it is generally known that Ar-OH produces ROOH by supplying H• to ROO•, and Ar-OH becomes phenoxyl radical (Ar-O•), which is relatively more stable, and stabilizes ROO•. The phosphorus-based antioxidant resolves ROOH to the more stable ROH, and the phosphorus-based antioxidant becomes oxidized and stabilizes ROOH.

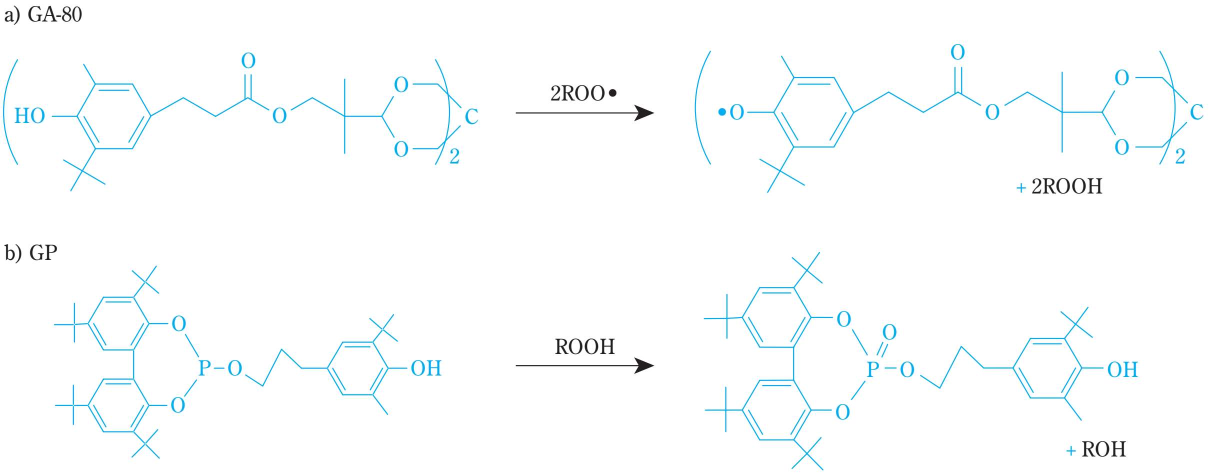
Stabilization Mechanism of G Series

Scheme 2 shows the basic stabilizing mechanisms of GP and GA-80 of the G series, which has been designed to suite the aforementioned polymer deterioration mechanism.

GA-80 is classified as Ar-OH. As shown in a) of **Scheme 2**, it supplies H• to ROO•, creating ROOH. GA-80 stabilizes ROO• by becoming a stable phenoxy radical. GP, on the other hand, is classified as a phosphorus-based antioxidant. As shown in b) of **Scheme 2**, it stabilizes ROOH by leading it to the stable ROH. GM/GS are R• scavengers, which are not classified among the phosphorus-based antioxidants. Their stabilizations will be described in a later section.

Changes in Customer Needs in Polymeric Additives Caused by Changes in the Market Environment

It is a conspicuous trend, in the polymer industry, to promote the differentiation strategy in order to survive the competition with rapidly rising large-scale delay manufacturers of the Middle East and China due to their strong cost-competitive power in terms of material scale and background. We can therefore assume that the direction of future customer needs can be summarized as follows:



Scheme 2 Basic stabilizing mechanism of GA-80, GP

(1) Environmental Response
  - Lighter weight, thinner film
  - Recycle, reuse

(2) Safety
  - Low elution (additives (bleed resistance), decomposition products of additives (hydrolysis resistance), resin having a low molecular weight)
  - Low transpiration (VOC, contamination of molds)
  - Work environment (measures to eliminate odor and fine particles)

(3) High Functionality and High Performance
  - Replacement with different materials
  - Resistance to discoloration/coloration

Sometimes more advanced polymer polymerization technology is required for a proper response to market needs. For example, higher processing temperature is required for thinner film extrusion, and therefore higher stabilization will be required. An increased amount of processing stabilizer might work, if the processing temperature isn't too high and the film isn't too thin. For use in food wrappings or electronic components, it is more necessary than ever that the additives, their decomposition products or polymers that have low molecular weight are not transferred to the food or the surface of the product, so that contamination of the product and/or the mold due to bleed-out will not occur. On the other hand, the differentiation strategy can often be a challenge in terms of the usage/processing conditions, which exceed the limits of conventional polymers. Therefore, in recent years the improvement of polymers and additives has increasingly been the solution to challenging cases.

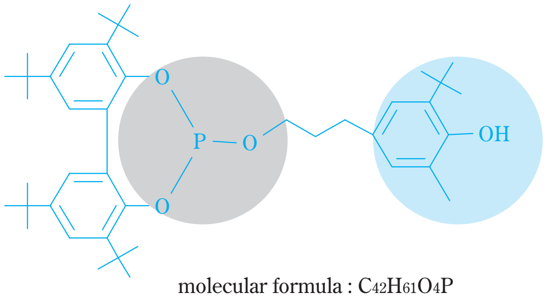
Contrastingly, it is a significant trend in the additive industry to enhance commodity antioxidants in response to the rapid increase of polymer production in China and the Middle East. However, these commodity antioxidants aren't necessarily adequate solutions for the improved stability of the more advanced polymers derived from the differentiation strategy.

The G series, which our company has developed, can be useful only when advanced stability is required. In order to meet such new customer needs, we have explored and developed the fields of application for the G series, and in the process we've proposed and provided solutions for our customers' differentiation strategies.

To introduce specific case examples of the G series and explain the reasons behind its unique performance, we have analyzed the G series' mechanism of action using GP and GS as examples. The results are introduced below:

Stabilization of Polyolefin by GP

GP is a high-performance, hybrid processing stabilizer independently developed and launched by Sumitomo Chemical Co., Ltd. in 2000 as an inhibitor of the fisheye gel that can be generated during the process of film-coating linear low-density polyethylenes (LLDPE) (**Fig. 1**). Conventionally, it has been common to use a phenolic antioxidant and a phosphoric antioxidant as processing stabilizers together for the LLDPE processing. The only phosphoric antioxidant available previously was the one having the three-valence phosphorus atom–which is the functional group for the ROOH stabilization–within its molecular structure (**Fig. 2**).



molecular formula : $C_{42}H_{61}O_4P$
molecular weight : 661
CAS No. : 203255-81-6

Fig. 1 Chemical structure of SUMILIZER® GP

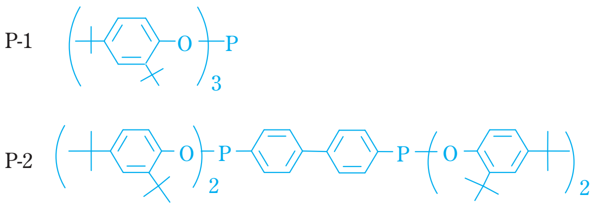


Fig. 2 Chemical structure of phosphite

Because GP has both the phenolic antioxidant part and the phosphoric antioxidant part within its molecules, it can be assumed that it quickly reduces the ROOH derived from ROO• to ROH. Therefore, GP significantly increases the process stability effect as compared to the combined application of a phenolic antioxidant and a phosphoric antioxidant.[2)]

Manufacturers have recently attempted to reduce the thickness of coating film as part of their environmental response activities. In order to achieve a thinner film coating, however, it is necessary to raise the process temperature. Therefore, fisheye gel tends to become more visible and more easily produced on LLDPE. For polypropylene (PP) also, it has been pointed out that the stability is not sufficient because phosphorus-based antioxidants are susceptible to thermal decomposition during the high-temperature process. Therefore, a high-performance processing stabilizer has been needed.

The examples of evaluation on two different cases (one using a phenolic antioxidant (AO-1) and a phosphorus-based antioxidant (P-1) together and the other using GP alone) of the high-temperature processing are shown below. **Figure 3** depicts the constitutional formula of the antioxidants used for this evaluation.

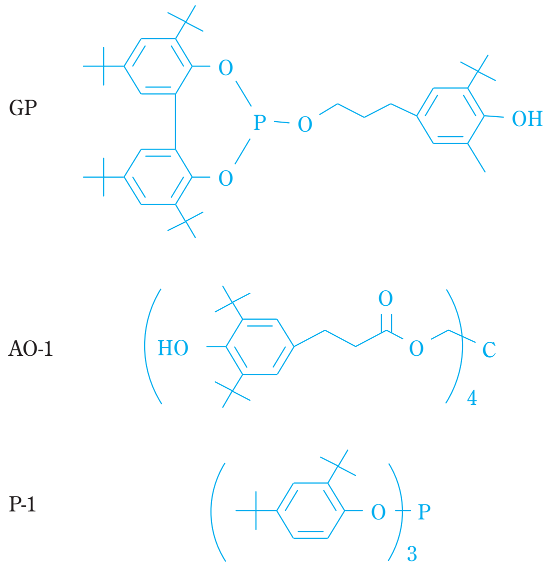


Fig. 3 Stabilizers used in this study

Figures 4 and **5** show the results of the following experiment to observe the stability of processing under high temperatures: Extrusion was repeatedly conducted at the temperatures of 250°C and 280°C. The pellets thus obtained were then compared in the MFR value, which is indicative of the resin flow.

Regarding PP, because molecular breakdown occurs due to the deterioration, a smaller MFR value signifies better performance.

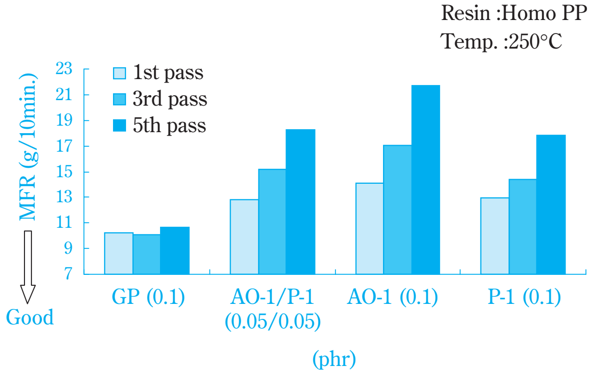


Fig. 4 Processing stabilization of GP when used alone

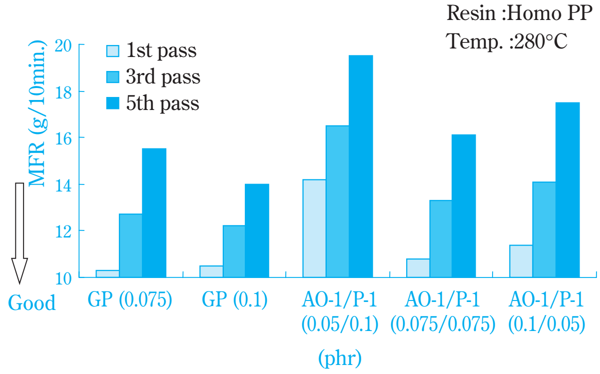


Fig. 5 Processing stabilization of GP in a low loading level

When using both a phenolic antioxidant (AO-1) and a phosphorus-based antioxidant (P-1) together, it is obvious that the change to the MFR after repeated extrusion at the temperature of 280°C was greater than that after repeated extrusion at the temperature of 250°C. This clearly means that the stabilization effect of AO-1/P-1 had deteriorated.

Conversely, the change to the MFR in GP after repeated extrusion at the temperature of 280°C is smaller than that in the AO-1/P-1 prescription, thus showing its outstanding processing stability even at higher temperatures. Additionally, shifting our attention to the loading level, the higher stability effect was achieved with a smaller loading level when using GP alone than when using both AO-1 and P-1. This indicates the fact that GP accommodates higher needs in regard to safety, in which both processing stability and lower elution (i.e., higher bleed resistance) are required. Moreover, the method by which to increase the loading level of the phenolic antioxidant having greater stability at a high temperature is known as the method that enhances processing stability. However, for phenolic antioxidants the processing stability MFR and the yellowing index YI are usually in a trade-off

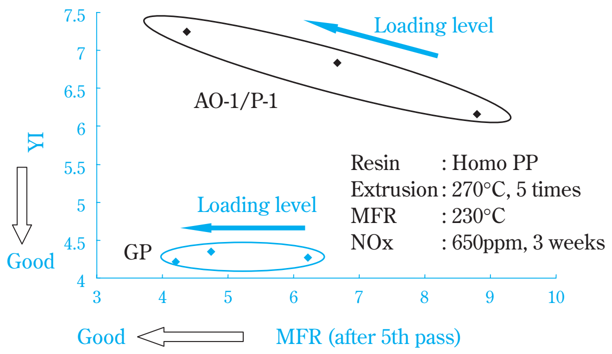


Fig. 6 Trade-off problem between MFR and YI

relationship. **Figure 6** shows the relationship between the color tone and processing stability after exposing PP to NOx gas.

It is obvious, as shown in **Figure 6**, that when the loading level is increased the YI value and level of coloration will increase under the AO-1/P-1 prescription as the processing stability improves. One can assume the reason for this is that the change has occurred to the colored item due to the oxidation of phenolic antioxidant. For example, the coloration mechanism analysis on dibutyl hydroxytoluene (BHT) has been well known for a long time. The phenolic antioxidant BHT becomes oxidized by NOx and produces quinone methides. Furthermore, it produces stilbene quinones and diaryl ethane. It is known that the stilbene quinones thus produced cause coloration.$^{3)}$

In addition to its outstanding MFR, it was also observed that although the processing stability of GP was improved by increasing the loading level, the increase in YI value was minimal. As a result of the structural analysis conducted on the reaction products of GP and NOx, it has been made clear that the reason for this is that, while GP has the phenolic part within its molecules, no reaction product has any color, thereby showing the high color-tone stabilization effect with respect to NOx (**Scheme 3**).

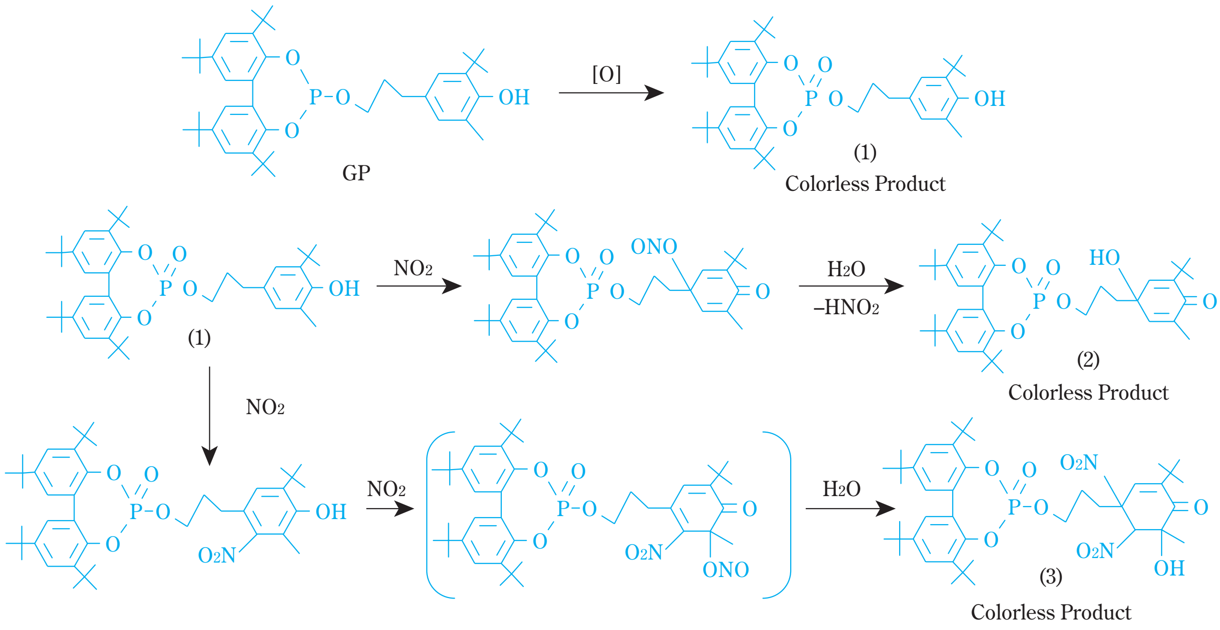
Stabilization Mechanism Analysis on GP

Thus GP improves the processing stability at high temperatures and smaller amounts. In order to analyze the mechanism by which GP manifests its outstanding processing stability, the contributions of the phosphorus part and the phenolic part have been inspected.$^{4)}$

First, in order to evaluate the reactivity between phosphorus-based antioxidants and peroxides, the reaction behaviors of GP and P-1 to cumene hydroperoxide) were analyzed as a model experiment. The results of this experiment are shown in **Figure 7**.

It has thus been demonstrated that GP quickly decomposes hydroperoxide and produces an oxidant of GP. However, P-1 decomposes hydroperoxide somewhat slowly, producing an oxidant of P-1. This indicates that GP decomposes cumene hydroperoxide more quickly than P-1 does.$^{5)}$

Secondly, to inspect the reactivity of GP with peroxyl radical as a phenol, the oxidation induction times



Scheme 3 Estimated reaction mechanism of GP with NOx

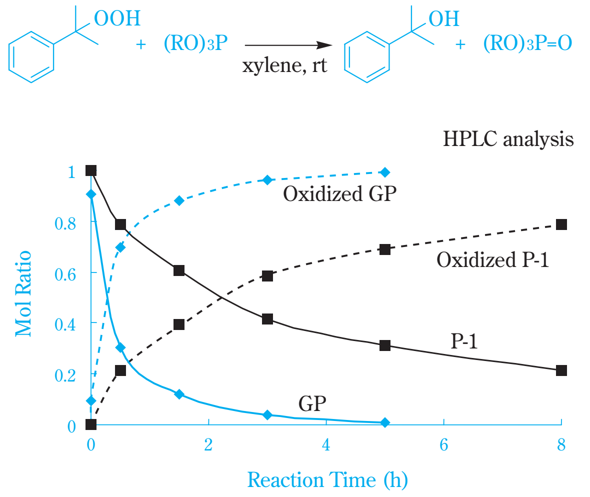


Fig. 7 Decomposition aspect of hydroperoxide with phosphite

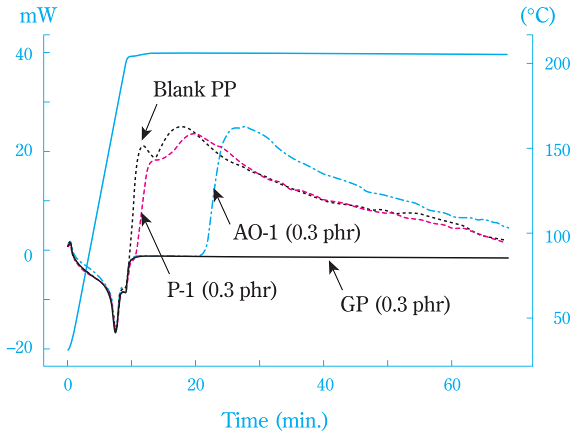


Fig. 8 Oxidation induction time (OIT) by DSC

(OIT) were measured. **Figure 8** shows the results of the OIT measurement conducted on the PP pellets containing AO-1, P-1 and GP.

In the pellet containing P-1 it became quickly oxidized and the endothermal peak was observed. The active species under this condition can be assumed to be a peroxyl radical. In other words, the longer the OIT is, the higher the reactivity with a polymer peroxyl radical will be.

The endothermal peak was observed on the pellet containing AO-1, but no such peak was observed on the pellet containing GP. This means that, while the pellet containing AO-1 was oxidized, the pellet containing GP was not at that point. In other words, GP can control the production of peroxyl radicals more effectively than AO-1, and demonstrates a high stabilization effect as a phenolic antioxidant.

Figure 9 shows the results of comparison of the amount of oxidants of the each antioxidant after being extruded three times.

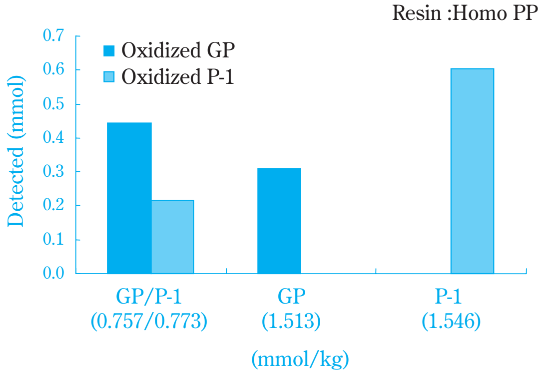


Fig. 9 Detected amount of oxidized antioxidants after extruded 3 times at 250°C

Although GP is highly reactive to peroxides, GP produces less oxidant from the antioxidant than P-1. This indicates that GP may act not only as a phosphite but also as a phenolic antioxidant.

Through the use of chemical substances having the similar frames, we inspected the advantage of having both the phenolic and phosphite parts within the molecules. **Figure 10** depicts the gelation time of each chemical substance after blending with resin.

It can be thought that because phosphites exist near the phenolic part in GP, ROOH is produced by sup-

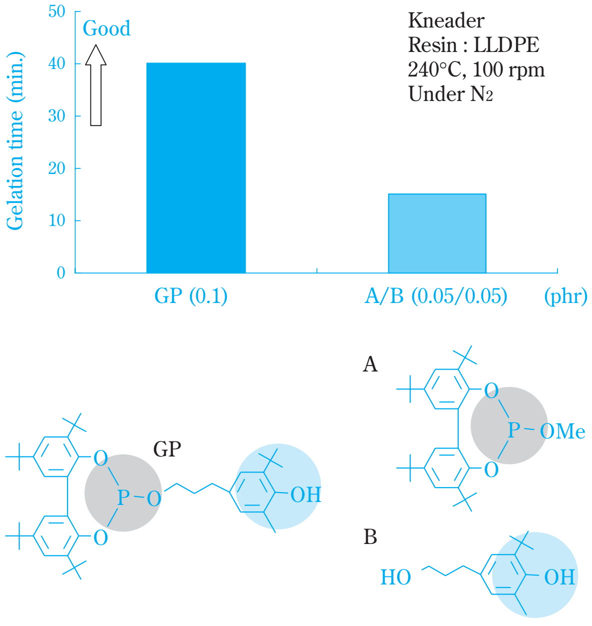


Fig. 10 Gelation time of phenolic and phosphonic moiety

plying the ROO• from the phenolic part to H•, thereby enabling a quick reduction.

On the other hand, when using the regular phenol and phosphites, since the phosphites aren't present in the vicinity of ROOH, it can be assumed that the reactivity is low. Therefore, part of the ROOH resolves without being reduced by phosphites, and other radicals are produced, resulting in polymer deterioration.

Summarizing the stabilization mechanism of GP, it has the phenolic part and traps the ROO• produced in polymers. GP also has a phosphite part and can reduce ROOH before RO• and •OH are reproduced. Accordingly, GP interrupts the auto-oxidation cycle and controls the production of ROOH and ROO•. It has been observed that GP demonstrates high stability when used alone. This is due to its molecular design, which has both the phenol and phosphite parts within the same molecule.

Growing Applications for GP

As a case example for the investigation of alternative applications of different materials, the application for rotational molding is reported below:

Rotational molding is the method of molding thermoplastic resin powders while rotating the mold on dual axes. The advantage of rotational molding is that large products can be molded, whereas products of such scale can't be achieved through injection molding or extrusion molding.

Currently, rotational molding is mainly used to create beverage tanks. However, because competition among manufacturers is expected to intensify in the future, the development of new applications for the purpose of differentiation has also begun (mainly in Europe). For example, taking advantage of resin's characteristic of facilitating complicated molding, the conventional materials were replaced with PE in order to mold products of complex shapes (e.g., highly creative furniture for which mold materials other than resin were previously used). While rotational molding has the advantage of being able to mold complex shapes such as curves, the disadvantage is that, because it is often performed under air, resin burn can occur. Therefore, a relatively large quantity of antioxidant must be used.

Because it is considered that color tone is extremely important in applications involving very creative products, antioxidants that are susceptible to coloration can't be used. Generally, and as shown in **Figure 6**, among the oxidants using the conventional technology, the better the performance is, the more susceptible to coloration it will be.

Assuming a rotational molding process, **Figure 11** shows PE's resistance against coloration using several antioxidants by exposing PE under high temperature and air for a long period of time (230°C, 40 minutes). It is clear that only the resin containing GP didn't turn yellow but instead maintained the initial color tone.

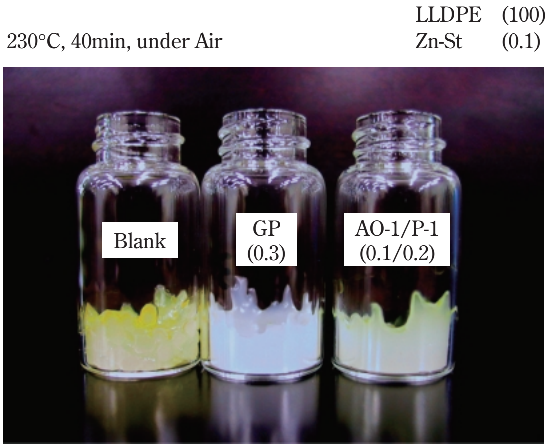


Fig. 11 Heat stabilization effect of GP

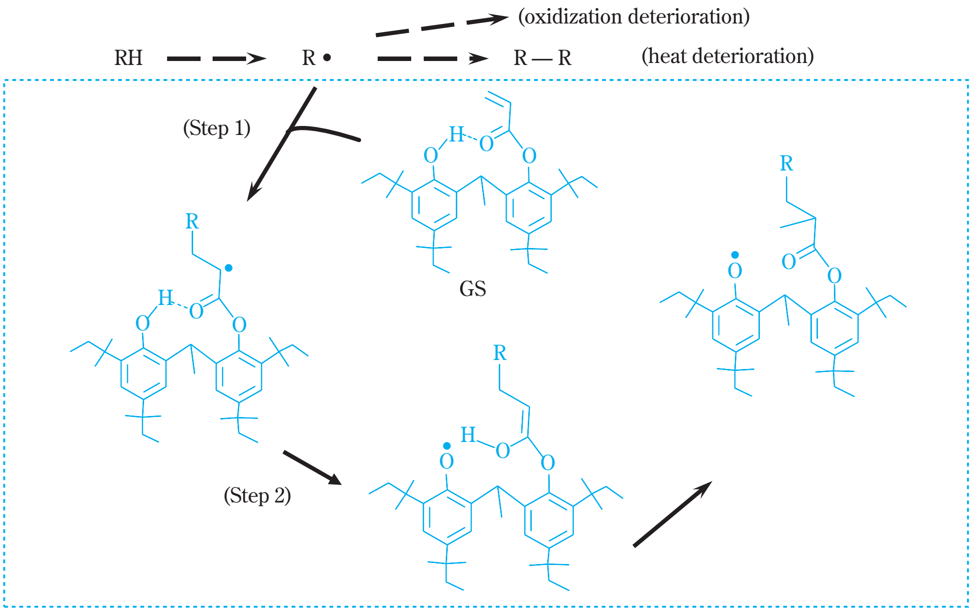
This signifies that GP demonstrates the outstanding effect of controlling thermal deterioration when molded using heat under air (i.e., rotational molding), thereby suggesting the potential of an expanded range of applications for GP.

Growing Applications for GS

Polyolefin (RH) produces alkyl radicals (R•) due to the action of heat. When R• has an adequate lifespan, the cross-linking reaction occurs due to the coupling of R• s, thus producing gel.

GS (GM) contributes to the stabilization by effectively trapping alkyl radicals under the mechanism shown in **Scheme 4**.

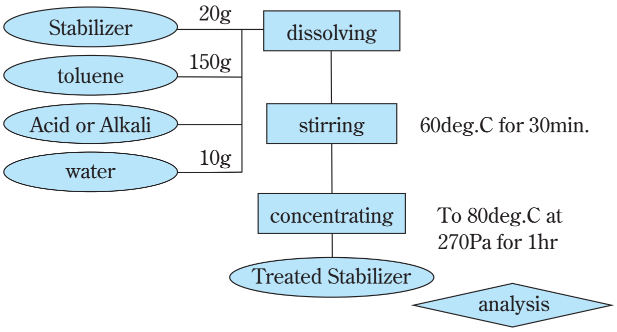
Generally, as shown in **Scheme 1**, it is more common to stabilize polyolefin with the ROO• produced by the reaction of R• to oxygen in the air, or with ROOH, which is one level above ROO•, instead of employing R•. However, when the principal chain becomes severed when processing polyolefin using high temperature to achieve higher molecular weight and a thinner wall, it is more effective to stabilize it with R•.



Scheme 4 Basic stabilizing mechanism of GS, GM

Thus the G series can stabilize all three of the deterioration types, which are of key significance in the deterioration mechanism of high polymers.

Although GS has a different action mechanism, it can be used together with the existing antioxidant under a certain condition or as a substitute of the existing antioxidant. For example, when a hydrolysis of the phosphorus-based antioxidant is the problem, a phenolic antioxidant alone is usually employed as a substitute. **Figure 12** shows the result of the stability test on GS and several typical phenolic antioxidants toward acid and alkali. The test procedure was as follows: After mixing the acetic acid, lithium acetate and lithium hydroxide water solutions with the stabilizers dissolved in toluene, they were stirred while heated. The recovery ratios of the stabilizers were then compared. As a result, it was found that GS was extremely stable toward both acid and alkaline water. However, because GS is strictly an R• scavenger but isn't an antioxidant, it can only be used as a processing stabilizer.



Retention (%) of purity after treatment (60deg.C for 30min.)

Stabilizer	CH_3COOH	CH_3COOLi	LiOH
GS	100.0	99.6	99.4
AO-1	99.6	97.6	90.3

Fig. 12 Hydrolytic Stability of GS

GS also has the function of trapping monomers. When molding polymers that have the depolymerization-type deterioration mechanism, such as polystyrene (PS), the monomer production derived from deterioration can cause issues such as mold contamination and/or the increased leaching of monomers from the product.

Figure 13 shows the result of the analysis on styrene monomer content using the injection-molded resin at a temperature of 300°C after dry-blending general-purpose polystyrene (GPPS) and the stabilizer into the resin and then extruding it at 230°C. GS showed a satisfactory result regarding the control of styrene monomer production, which occurs during the high-temperature processing.

No effect was observed on AO-2 despite the increased amount of loading, but it has been demonstrated that GS reduces the styrene monomer content to half of that observed when using AO-2 at 0.2phr.

It can be said that these results meet the customer needs, whereby they are considered essential effects from the perspective of environmental response.

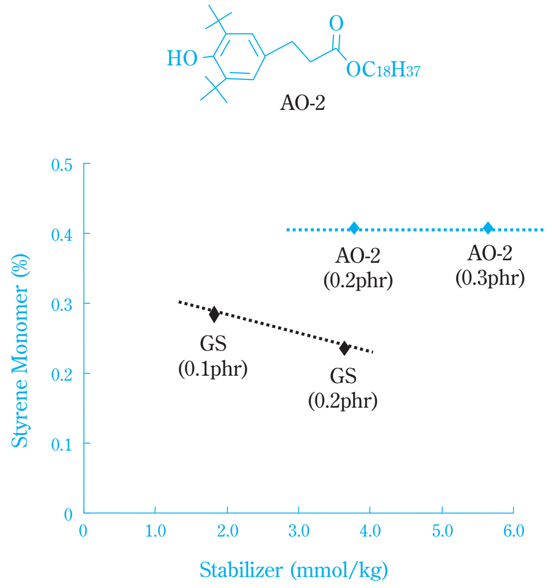


Fig. 13 Effect to reduce Styrene Monomer

However, GS can cause a delay in polymerization due to its outstanding effect when added during the polymerization process. For this reason it is necessary to pay careful attention to the accumulation in the recovery system during the process.

Development of New High-Performance Stabilizers

Styrene-butadiene copolymer (SBS) has the characteristic of deteriorating when it is heated during processing, so that cross-linking occurs in the butadiene part. Combining with R• scavengers such as GM/GS, it is also used for shrink films for PET bottles, for which the control of extremely minute "bubbles" is required. However, the reduction of fisheye gel is required at a higher level due to the recent trend toward more complicated shapes, higher creativity and thinner film coatings. From the greater interest in environmental issues, on the other hand, if SBS is processed at a higher temperature in order to further reduce the amount of solvent remaining in the resin, the occurrence of cross-linking increases. Even more advanced cross-link control technology is in demand for the "battle" between butadiene and cross-linking (which can be viewed as the "destiny" of butadiene-type polymers).

Our proprietary product, GS, has the incomparably unique function of protecting polymer from cross-linking by trapping alkyl radicals (refer to **Scheme 4**), and this function has facilitated its rapid growth in the market. Today, it is a pressing need to develop such outstanding processing stabilizers that have even higher performance as needed to accommodate the latest requirements of higher quality and transpiration resistance.

GS has the incomparably unique function of protecting polymer from cross-linking by trapping alkyl radicals.

Table 2 shows the result of the mixing test on SBS resin using a Labo-plastmill. The use of such a mill enables us to readily and quantitatively understand the processing-stabilization performance by observing the changes to the torque of the polymer.

Table 2 Build-up time of X

SBS (100phr)	250°C
additive (0.5phr)	Build-up time (min.)
GS	43
X	121

Concerning SBS resin, the longer it takes to reach the torque peak the more slowly the deterioration will progress. From this experiment it has been found that polymer additives that can extend the time for polymers to reach the torque peak have better processing-stabilization performance.

As shown in **Table 2**, it has been demonstrated that the development X can extend, by a factor of three, the time required to reach the torque peak as compared to GS. This suggests that X can provide the higher processing stability needed for the control of cross-linking in butadiene.

We will, from this point forward, continue our development of new products that can accommodate customer needs by optimizing their chemical structures.

Conclusion

We are planning to expand the potential of GP, not only as a stabilizer for LLDPE but for other areas as well. In order to achieve this goal, we will look toward the expansion of overseas sales and broader applications to the peripheral areas based on the actual results of applications to PP and HDPE. Making the most of our molecular design technology, processing evaluation technology and design technology for the mixture proportions obtained during the development of the G series to date, we at Sumitomo Chemical Co., Ltd., hope to contribute to society by developing high-performance stabilizers that accommodate customer needs, as required by the technical innovation of polymers.

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