Effect of raw-material stabilization on adhesive quality

G. Knobloch, H. Martin, A. Patel, and P. Rota Graziosi

Adhesives of consistent quality can be obtained by stabilizing raw-material components with a suitable antioxidant.

Adhesive formulations contain various components—polymers, tackifier resins, waxes, oils—all of which are susceptible to thermoxidative degradation. While the nature of this degradation usually differs from one component to another, the negative effects of degradation are carried over into the adhesive formulation.

Antioxidants are typically added to adhesive formulations in an effort to protect them from degradation. However, the protective effect of the antioxidants can be impaired and even cancelled if the adhesive components have suffered degradation before the adhesive is formulated. Adhesive formulators can manufacture products of consistently high quality by using raw materials that have been stabilized to resist degradation by heat. This is especially important in today's manufacturing environment, where many companies are working with statistical process control (SPC) and statistical quality control (SQC).

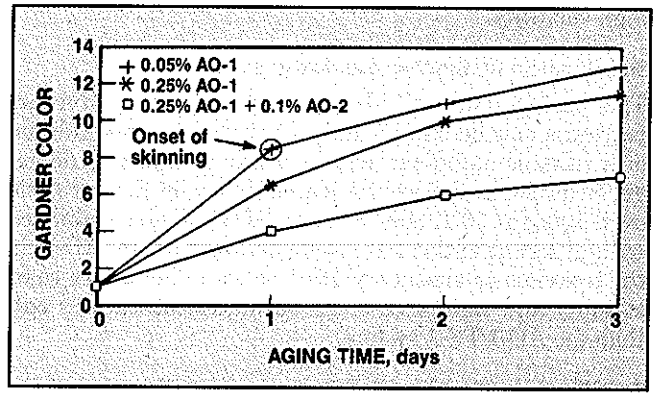
This article examines the role of stabilizers in the manufacture of high-quality adhesives. **Table I** lists the various antioxidants and co-additives used in this study. The results indicate that:

- Components of high quality and consistently superior properties can be obtained by adding an effective stabilizer system at an early stage of production.
- The quality of raw materials can be retained during storage and processing by the addition of adequate and effective stabilizer systems.
- The use of well-stabilized ingredients is a basic requirement for the production of high-quality adhesives.

I. Antitoxidants and co-additives

AO-1	2,6-di-t-butyl-4-methylphenol
AO-2	Tetrakis[methylene(3,5-di-t-butyl-4-hydroxyl-hydrocinnamate)]methane
AO-3	2,4-bis-(N-octylthio)-6-(4'-hydroxy-3',5'-di-t-butyl-anilino)-1,3,5-triazine
AO-4	2,4-bis[(octylthio)methyl]-o-cresol
AO-5	Triethyleneglycol-bis-3-(3'-t-butyl-4'-hydroxy-5'-methylphenyl)propionate
AO-6	Butylated reaction product of p-cresol and dicyclopentadiene
AO-7	Hindered phenol
AO-8	Octadecyl-3-(3',5'-di-t-butyl-4'-hydroxy-phenyl)propionate
AO-9	2,2'-methylenebis(4-methyl-6-t-butylphenol)
AO-10	Zinc dibutyldithiocarbamate
PS-1	Trisnonyl-phenylphosphite

1. Discoloration of EVA during oven aging at 170°C



Stabilization of polymers used in adhesive formulations

The polymers used in the production of adhesives are usually treated with a minimal amount of stabilizer to help them withstand the effects of isolation, drying, and warehouse storage. In many cases, however, polymer performance can be dramatically improved by supplementing this dose with a small amount of the right stabilizer.

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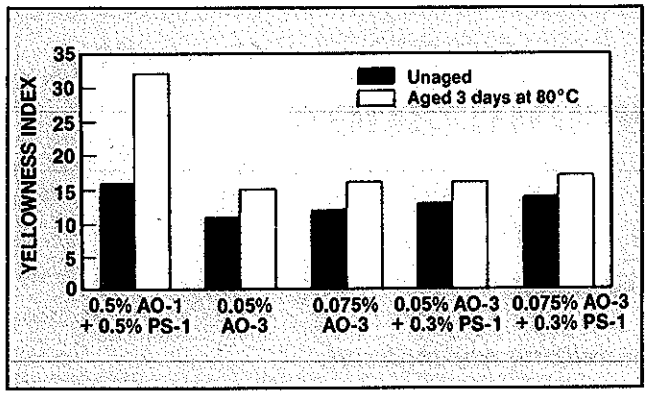
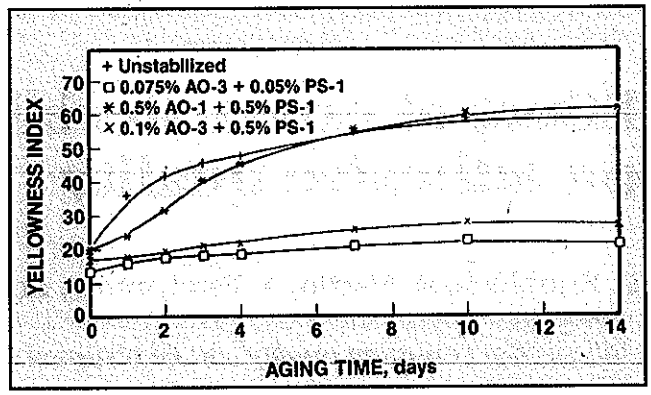
Stabilization of EVA polymer

Figure 1 shows the color response of a commercially available EVA (ethylene vinyl acetate) polymer during

2. Discoloration of SIS during oven aging at 80°C. (Aging of 2-mm plates on glass plates.)



3. Discoloration of SIS during oven aging at 80°C. (Aging of 2-mm plates on glass plates.)

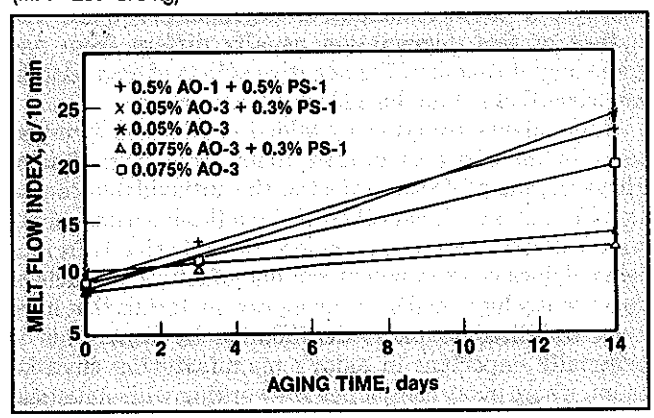


static oven aging at 170°C (338°F). The addition of AO-2 significantly reduced the amount of discoloration and completely prevented skin formation, even after three days of high-temperature aging. This performance probably would have been improved further if AO-2 had been added during polymerization. The addition of AO-2 also significantly increases the stability of EVA polymers during dynamic aging. The use of AO-2 instead of AO-1 would lead to a simple and superior stabilization for EVA hot melts.

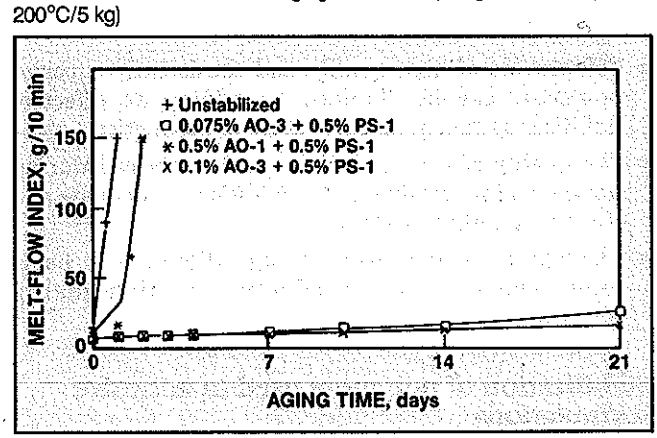
Stabilization of SIS thermoplastic elastomers

Figures 2–5 illustrate the effects of AO-1, AO-3, and PS-1 on the performance of SIS (styrene-isoprene-styrene) polymer during static oven aging at 80°C (176°F). As seen in Figs. 2 and 3, AO-3—either alone or in combination with PS-1—provides significantly better color stability than the AO-1/PS-1 system. The same results are evident in Figs. 4 and 5, which depict melt-flow index (MFI) stability over time. The MFI was determined after aging the polymer in a closed system. Rubber samples were wrapped in aluminum foil and placed in screw-top bottles. This aging procedure, which was intended to simulate the conditions of silo storage, favored AO-1, which is well known for its high volatility.

4. Melt-flow index of SIS after aging at 80°C in closed glass bottles. (MFI—200°C/5 kg)



5. Melt-flow index of SIS after aging at 80°C in open glass bottles. (MFI—200°C/5 kg)



Stabilization of SBS thermoplastic elastomers

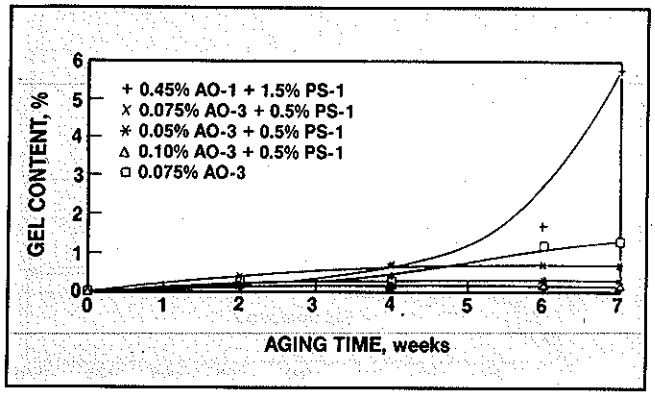
The performance of SBS (styrene-butadiene-styrene) polymers can be significantly improved by the addition of a suitable stabilizer system. **Figures 6 and 7** depict gel formation and discoloration, respectively, during static oven aging at 70°C (158°F) of an SBS polymer stabilized with different antioxidant systems. Here again, AO-3, in the presence or absence of PS-1, leads to far better color stability and resistance to gel formation at a lower cost than the AO-1/PS-1 system.

Stabilization of carboxylated styrene-butadiene latex

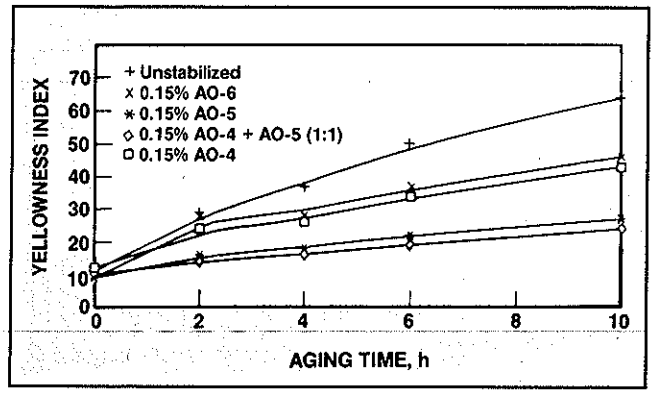
The three polymers mentioned so far—EVA, SIS, and SBS—are materials that are used by the hot-melt industry or, sometimes, in solvent-based adhesives (SIS and SBS). The same stabilizing influence can be imparted to other polymers, such as the latices used in water-based adhesives.

Figures 8 and 9 illustrate the discoloration of 0.25-mm carboxylated SBR (styrene-butadiene rubber) latex films during oven aging at 150°C (300°F). Both AO-4 and AO-5 showed a significantly greater stabilizing effect than the classical antioxidants. The combination AO-4/AO-5 (1:1 ratio) was the most effective system for both latices. The discoloration of a latex film is related to its mechanical properties (embrittlement, tensile strength, elongation) as well as its adhesive properties. Thus AO-4, AO-5, and the AO-4/AO-5 blend would significantly improve the

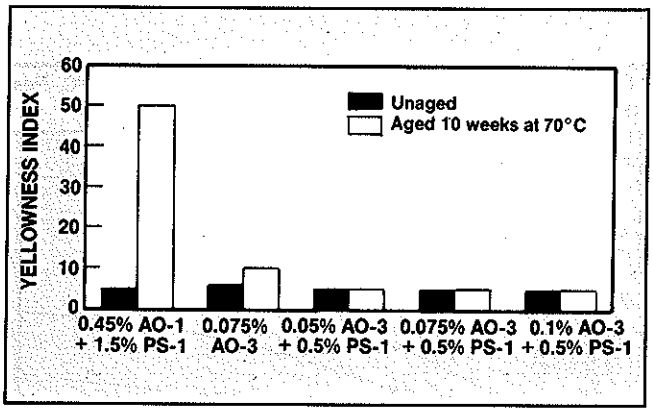
6. Gel content of SBS after aging at 70°C. (Gel content = insoluble polymer in toluene at 20°C.)



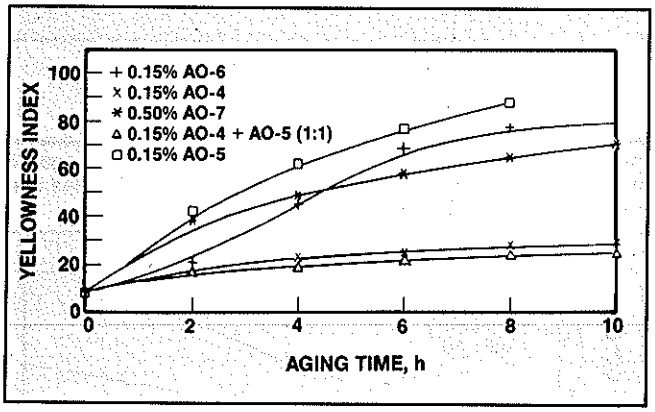
9. Discoloration of X-SBR latex B during oven aging at 150°C



7. Discoloration of SBS after aging at 70°C



8. Discoloration of X-SBR latex A during oven aging at 150°C



performance of an adhesive formulation based on such a latex.

Stabilization of hydroxyl-terminated polybutadiene

Liquid hydroxyl-terminated polybutadiene is used to produce polyurethane sealant. Storage of this material at high temperatures can lead to gel formation, increased viscosity, and discoloration. **Figure 10** illustrates the influence of AO-3 and AO-8 on gel formation and viscosity change during oven aging at 65°C (149°F). The viscosity of the unstabilized sample starts to rise after less than 15 days, with gels appearing after approximately 40 days. The samples stabilized with AO-3 and AO-8 show only limited or no increase in viscosity, and there was no trace of gel after more than 200 days aging.

Figure 11 presents discoloration results obtained during the study of various antioxidants on the hydroxyl-terminated polybutadiene. AO-8 delayed the onset of polymer discoloration, while the polymer treated with AO-9 and AO-10 exhibited strong yellowing. As a result, AO-8 was selected for use in a study of polyurethane sealant, the results of which are presented later in this article.

Stabilization of tackifier resins

Tackifier resins are extremely sensitive to thermoxidative degradation. Some of them degrade rapidly even at room temperature. Oxidation of tackifier resins causes undesirable changes in melt viscosity, softening point, compatibility, and other physical and chemical properties. This can strongly influence the properties of the final adhesive.

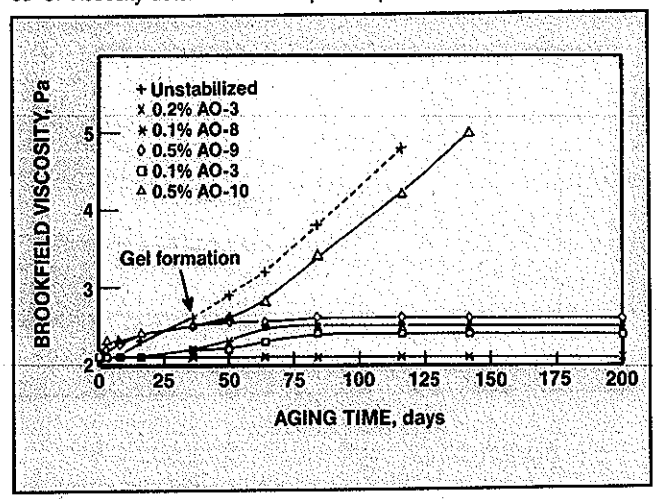
Tackifier degradation during storage can be minimized through use of effective stabilizers. The mechanism of tackifier oxidation follows the well-known scheme of autoxidation summarized in **Fig. 12**. Degradation can be monitored by measuring hydroperoxide formation before—and color development and viscosity after—melting of the resin.

Stabilization of rosin ester resins

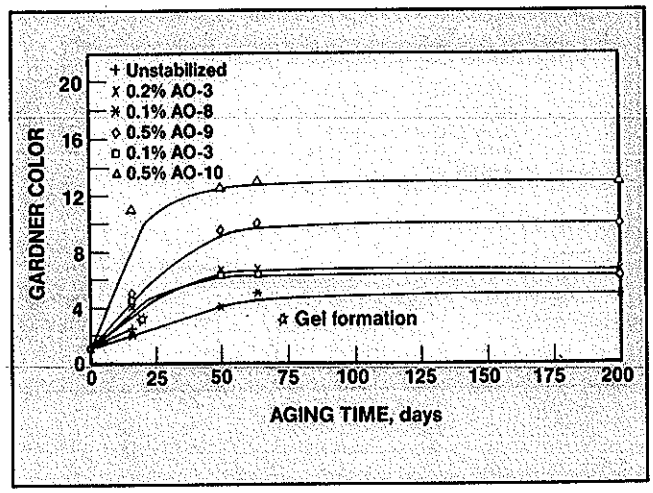
Hydroperoxide formation. A representative sample of ground rosin ester was placed in an open Petri dish and stored at 40°C. **Figure 13** shows that the rate of hydroperoxide formation was slowed considerably by addition of AO-2 and AO-3.

Discoloration. The hydroperoxides, being relatively stable at ambient temperature, decompose spontaneously at temperatures commonly used during hot-melt compounding or during drying of solvent- and water-based adhesives. The decomposition products initiate further reactions, leading to colored species. Since AO-2 and AO-3 reduce the formation of hydroperoxides, they also should reduce the discoloration of the resin after storage. This is confirmed by the results in **Fig. 14**.

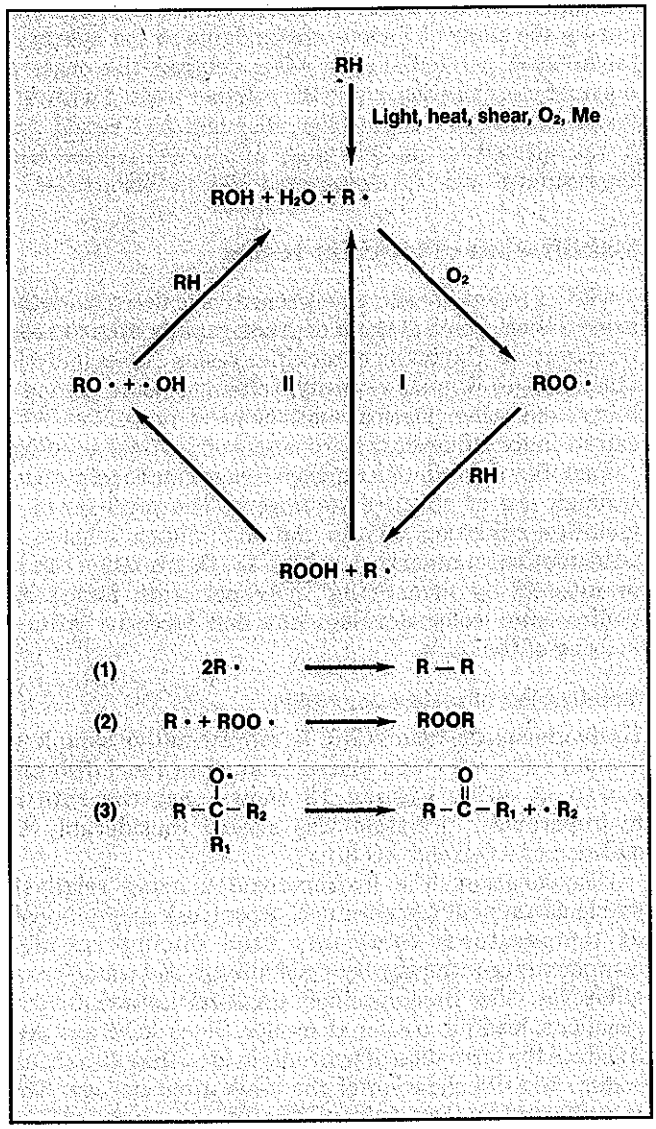
10. Viscosity of liquid hydroxyl-terminated polybutadiene during aging at 65°C. Viscosity determined at 10 rpm in Spindle 21



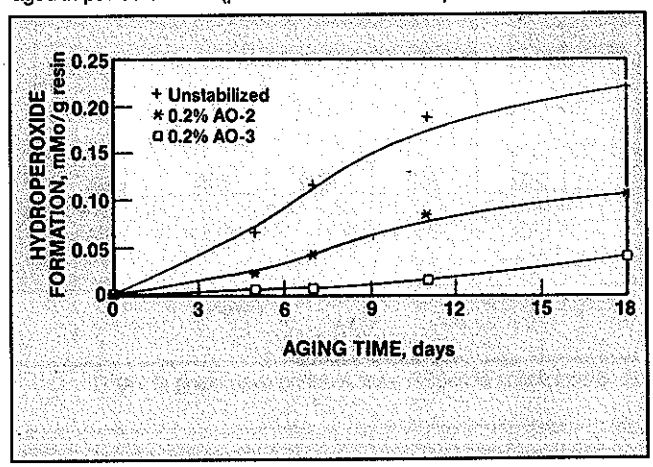
11. Discoloration of liquid hydroxyl-terminated polybutadiene during aging at 65°C



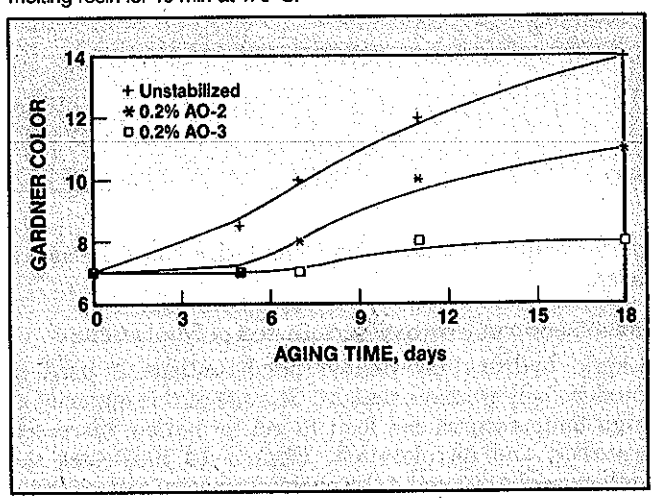
12. Autoxidation mechanism



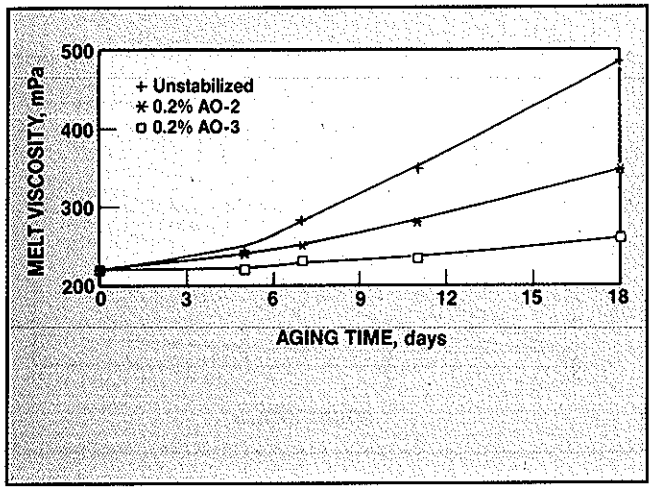
13. Hydroperoxide formation in rosin ester while aging at 40°C. Resin aged in powdered form (particle size 0.1–0.8 mm)



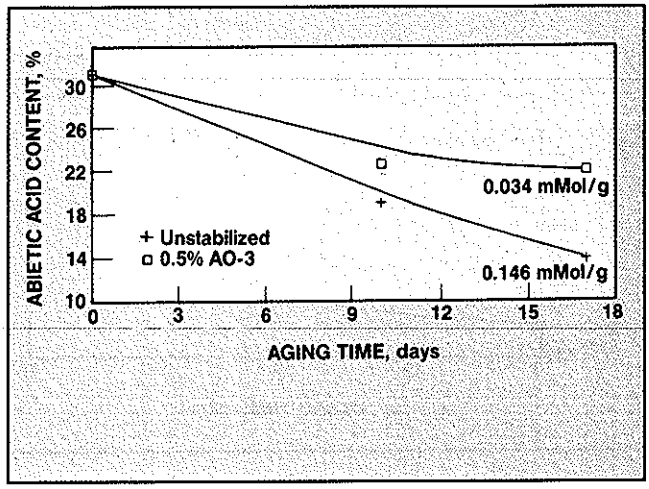
14. Discoloration of rosin ester while aging at 40°C. Resin aged in powdered form (particle size 0.1–0.8 mm). Color was determined after melting resin for 10 min at 170°C.



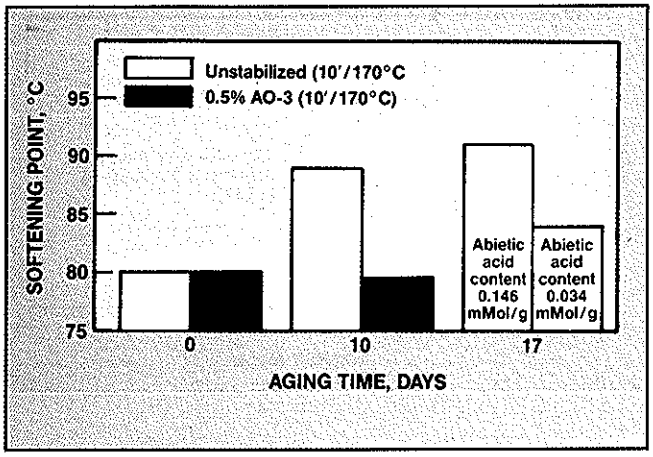
15. Melt viscosity (at 170°C) of rosin ester after aging at 40°C. Resin aged in powdered form (particle size 0.1–0.8 mm)



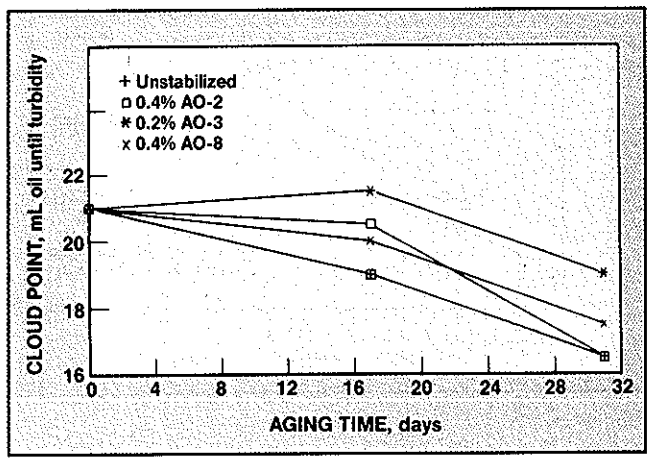
16. Abietic acid content of gum rosin while aging at 40°C. Rosin in powdered form



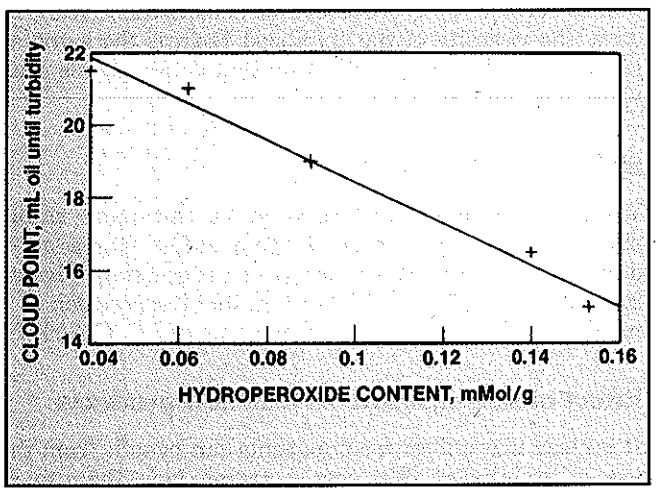
17. Softening point (R&B) of gum rosin during storage at 40°C



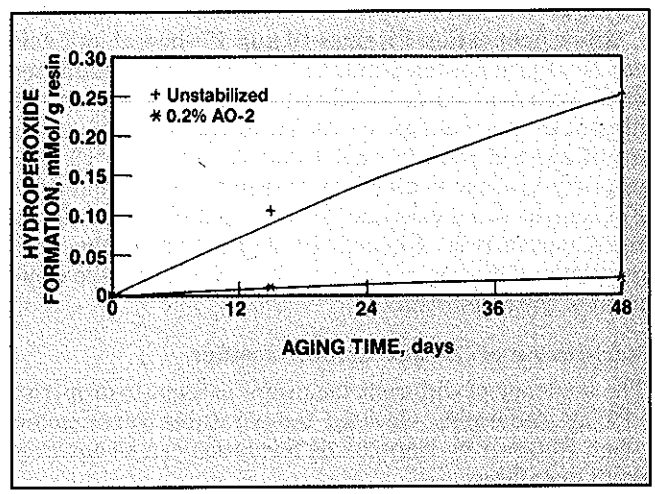
18. Cloud point of phenolic-modified rosin resin during storage at 40°C. Oil: Haltermann PKWF 6/9AF new



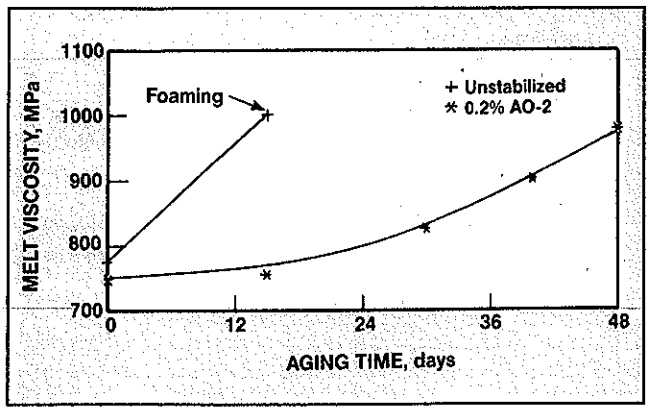
19. Cloud point as a function of hydroperoxide content for phenolic-modified rosin resin



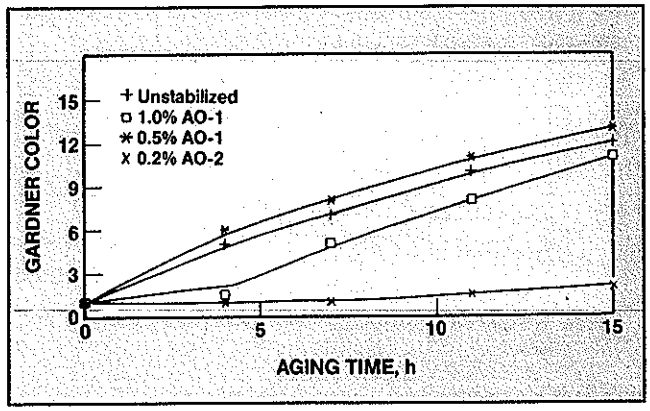
20. Hydroperoxide formation in C5-hydrocarbon tackifier resin while aging at 40°C. Resin aged in powdered form (particle size 0.1–0.8 mm)



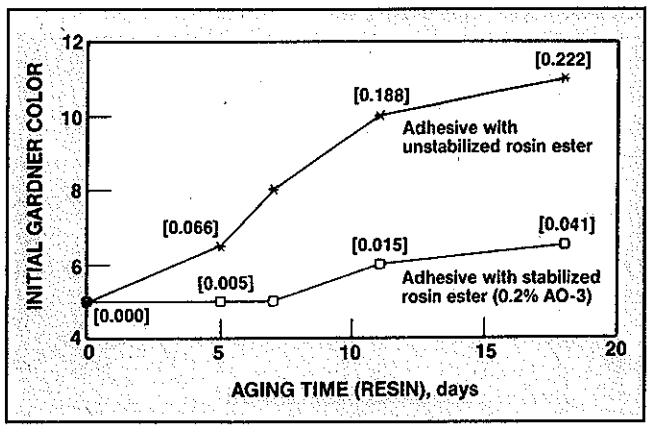
21. Melt viscosity (at 170°C) of C5-hydrocarbon tackifier resin while aging at 40°C. Resin aged in powdered form (particle size 0.1–0.8 mm)



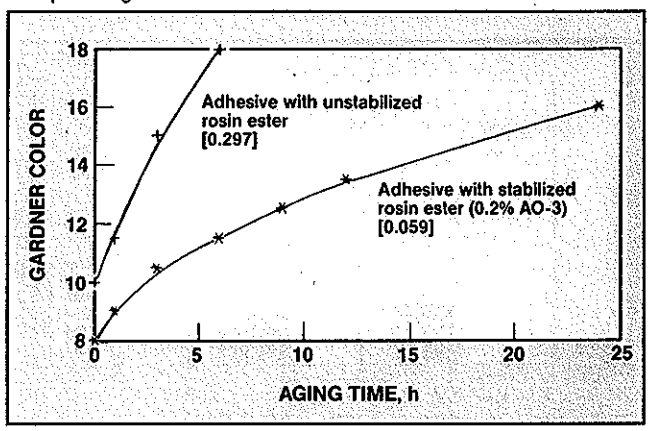
22. Discoloration of microcrystalline wax while aging at 177°C



23. Influence of resin quality on color of EVA hot-melt adhesive. Resin aged at 40°C. The numbers in brackets represent the resin's hydroperoxide content (mMol/g) before compounding.



24. Influence of resin quality on color of EVA hot-melt adhesive aged at 170°C. Resin aged 18 days at 50°C before compounding. The numbers in brackets represent the resin's hydroperoxide content (mMol/g) before compounding.



Melt viscosity. The melt viscosity of the rosin ester affects the processability and end-use performance of the final adhesive. In most cases, the melt viscosity correlates with the hydroperoxide content of the rosin ester. The results in **Fig. 15** confirm that AO-2 and AO-3 minimize the increase in melt viscosity of resin stored at 40°C (104°F).

Other properties. Figures 16 and 17 show abietic acid content and softening point, respectively, for unstabilized gum rosin and rosin stabilized with AO-3. **Figure 18** illustrates the change in "cloud point" of a phenolic-modified rosin resin during storage at 40°C (104°F). This property is of particular importance to the ink industry. Figures 16–18 indicate that AO-3 is effective in stabilizing rosin derivatives. **Figure 19** demonstrates the good correlation between hydroperoxide content and the cloud point of the rosin resin.

Stabilization of C5-hydrocarbon tackifier

The tendency of different tackifiers to form hydroperoxides at moderately elevated temperatures varies somewhat. However hydroperoxide formation can be observed in all tackifiers.

Figure 20 shows that AO-2 significantly inhibits formation of hydroperoxide in C5-hydrocarbon resins. **Figure 21** shows that AO-2 has a similar effect on melt viscosity. After 15 days aging at 40°C (104°F), the unstabilized resin starts foaming upon melting. (Figure 12 suggests that this foaming occurs because of the water that is formed as hydroperoxides decompose.) After 15 days, the viscosity of the stabilized resin is the same as it was on the first day, indicating that it can still be used without quality problems.

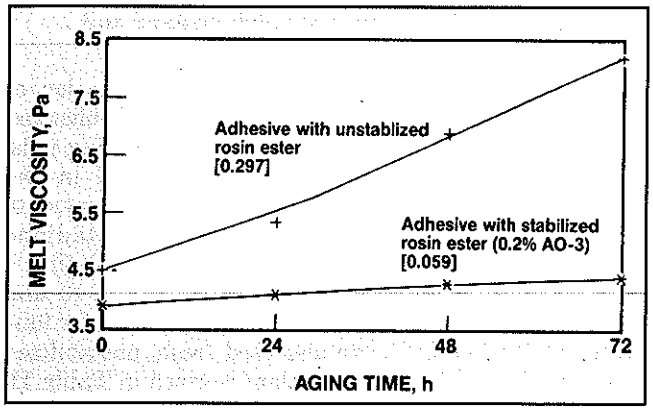
Stabilization of waxes

Waxes are usually considered to be thermally stable materials. However, most of them suffer degradation during high-temperature storage and processing. **Figure 22** shows the influence of AO-2 on the discoloration of a microcrystalline wax during oven aging at 177°C (350°F).

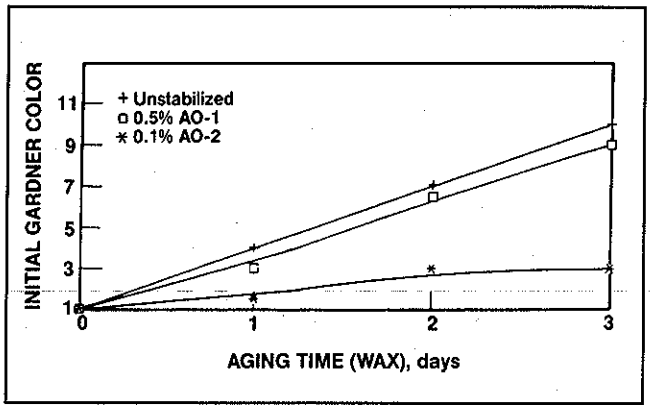
Effect of stabilization on finished products

It is clear that adhesive components can benefit from the use of stabilizers. We now examine how the use of

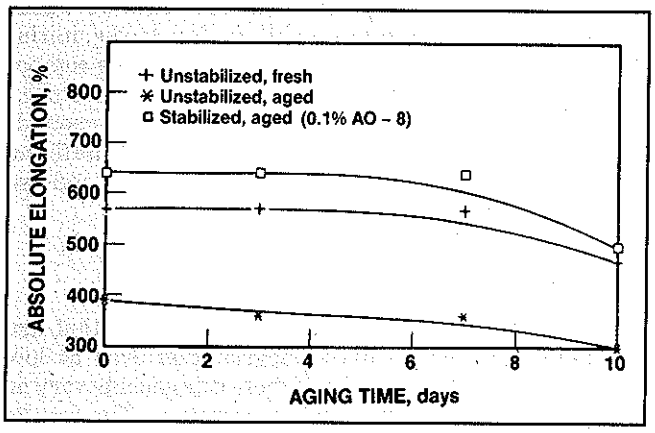
25. Influence of resin quality on melt viscosity (at 170°C) of EVA hot-melt adhesive aged at 170°C. Resin aged 18 days at 50°C before compounding. The numbers in brackets represent the resin's hydroperoxide content (mMol/g) before compounding.



26. Influence of microcrystalline wax quality on initial color of EVA hot-melt adhesive. Wax aged at 150°C



27. Influence of hydroxyl-terminated polybutadiene quality on elongation of polyurethane sealant aged at 80°C. Polybutadiene aged 4 weeks at 50°C before formulation.



II. Polyurethane formulation

Hydroxyl-terminated polybutadiene	100
Short-chain diol	3
Plasticizer	75
Filler	150
Antifoam agent	0.2
Silane	2
Catalyst	0.04
Isocyanate	16.2

stabilized components affects the properties of the finished product.

Stabilized tackifiers and quality of EVA hot-melt adhesives

Stabilized and unstabilized glycerol rosin ester tackifiers were aged and then used as components in an EVA hot-melt adhesive. The adhesive formulation contained EVA, tackifier, and wax in a 1:1:1 ratio. These components were melted together under stirring in an open beaker at 177°C (350°F).

Initial color of adhesive. Figure 23 shows the effect of tackifier storage time at 40°C (104°F) on the initial color of the EVA hot-melt adhesive. The adhesive containing the unstabilized resin undergoes substantial discoloration as tackifier storage time increases (i.e., as hydroperoxide content increases). The stabilized tackifier has a negligible effect on the initial color of the adhesive, even in the case of aged resin. Figure 23 shows that while addition of antioxidant reduces discoloration, it cannot improve the initial color of the hot melt. Antioxidants cannot reverse the negative effect of hydroperoxide-containing resins.

Discoloration of adhesive. Figure 24 illustrates the effect of high-temperature aging (170°C) on the color of a hot-melt EVA formulated with stabilized and unstabilized tackifier. The tackifier was aged first in powder form (50°C, 18 days) and then under stirring in an open beaker at 177°C (350°F). The results of the aging test clearly show that the use of an unstabilized, degraded tackifier resin leads not only to a darker initial color but also to a much faster discoloration of the hot melt under high-temperature conditions compared with a stabilized tackifier that has been minimally damaged.

Viscosity change of adhesive. Figure 25 shows that the melt viscosity of the EVA hot-melt adhesive made with the aged, unstabilized tackifier increased substantially under high-temperature (170°C) conditions. The increase in melt viscosity was much smaller for the adhesive formulated with tackifier resin that was stabilized before being aged.

Stabilized wax and quality of EVA hot-melt adhesives

EVA hot-melt adhesives were formulated using stabilized and unstabilized waxes that had been aged at 150°C. **Figure 26** shows that the initial color of EVA hot-melts was lower in the case of adhesives made with wax that

had been stabilized with small amounts of AO-2. Application of relatively large quantities of AO-1 improved performance, but only slightly.

Stabilized hydroxyl-terminated polybutadiene and quality of polyurethane sealants

Earlier in this article we showed that stabilization of hydroxyl-terminated polybutadiene with AO-8 enhanced color and viscosity performance while eliminating gels. Hydroxyl-terminated polybutadiene is used in the manufacture of polyurethane sealant. We attempted to determine how stabilization of this polybutadiene component affected the final product by formulating a polyurethane sealant using stabilized (0.1% AO-8) and unstabilized materials that had been warehoused for four weeks at 50°C (122°F). We also used fresh, unstabilized material. The recipe for the sealant is given in **Table II**. The polyurethanes were then oven-aged for 10 days at 80°C (176°F).

Figure 27 illustrates the variation of elongation after oven aging. The polyurethane produced with the stabilized polybutadiene exhibits the same elongation as the polyurethane produced with the fresh, unstabilized polybutadiene. The sealant obtained with the aged, unstabilized polybutadiene exhibits far lower initial elongation. This indicates that the polybutadiene component was damaged during the aging at low temperature.

The addition of a suitable antioxidant during compounding further improves the heat stability of polyurethane sealants. The best antioxidants systems for this end-use stabilization are AO-4 and AO-2.

Conclusion

Adhesives are formulated from raw materials that are susceptible to thermoxidative degradation even at low temperatures. The properties of these components vary as a function of storage time and temperature. The results presented here indicate that:

- Unstabilized raw materials tend to lose their initial properties during storage at low temperature and during processing at high temperature.
- The effective life of adhesive components can be extended by adding an appropriate antioxidant at an early stage of production.
- The use of stabilized components improves adhesive quality.□

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