

Mechanism of Ultraviolet Stabilization of Polymers by Aromatic Salicylates*

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Synopsis

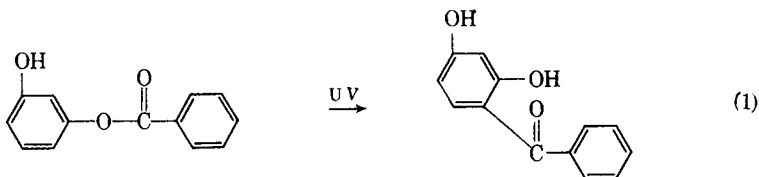
Many derivatives of phenyl salicylate turn yellow when they are exposed, in solution, to ultraviolet light. This limits their usefulness as ultraviolet stabilizers for plastics. Evidence is presented to support the postulation that the yellowing is due to the formation, by a photochemical *ortho* rearrangement, of a derivative of 2,2'-dihydroxybenzophenone. Aromatic salicylates, such as 2,6-dialkylphenyl salicylate, in which the *ortho* rearrangement is blocked, are found to be nonyellowing stabilizers, although less effective than the better yellowing varieties, such as *p*-octylphenyl salicylate. Loss of stabilizer by volatilization, either in compounding or during subsequent exposure, is shown to be an important factor in limiting the effective performance of the stabilizer.

Introduction

The aromatic salicylates—phenyl salicylate (salol), *p*-*tert*-butylphenyl salicylate (TBS) and *p*-*tert*-octylphenyl salicylate (OPS)—are well-known, commercially useful, ultraviolet stabilizers for plastics. For example, the addition of 1% of salol to a sheet of cellulose acetate butyrate 50 mil thick extends its useful outdoor life in Kingsport, Tennessee, from 6 months to about 4 years. Addition of OPS to polyethylene produces a similar improvement in weatherability.

Exposure of these stabilized plastics to sunlight is accompanied by a yellowing reaction which is more pronounced with OPS than with salol. Meyer and Gearhart² observed a yellowing of both salol and its isomer, resorcinol monobenzoate (RMB), when these compounds were irradiated with a S-1 sun lamp, either in isopropyl alcohol or in cellulose acetate butyrate plastic. The photochemical reaction taking place in the case of RMB has since been explained³ as a photorearrangement to a third isomer, 2,4-dihydroxybenzophenone. This is shown in Figure 1, which illustrates the conversion of RMB to the benzophenone during exposure under an RS-275 sun lamp in cellulose acetate butyrate film. The reaction mechanism is postulated to be a photo-induced *ortho* rearrangement of the Fries type, as indicated in eq. (1).

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Anderson and Reese⁴ have described a similar photorearrangement of catechol monoacetate. Kobsa⁵ has recently applied such photorearrangements to the practical synthesis of a variety of benzophenone derivatives from the corresponding phenyl benzoate derivatives.

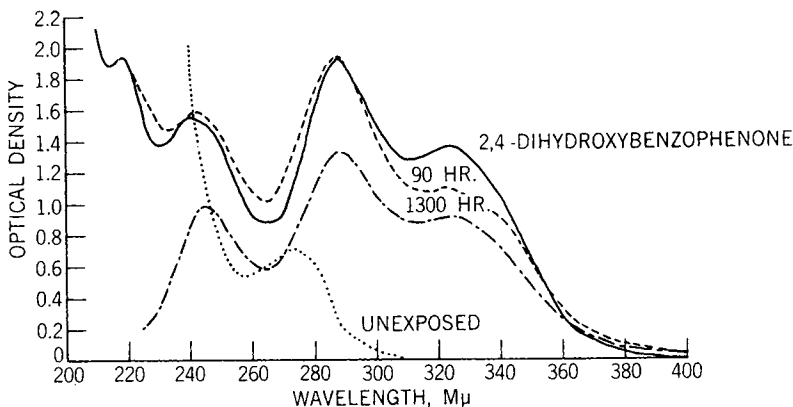
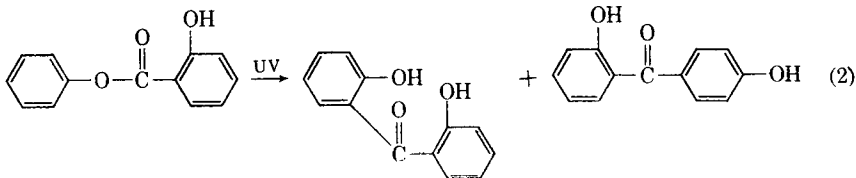


Fig. 1. Photochemical conversion of resorcinol monobenzoate.

If the yellowing observed on ultraviolet exposure of the salicylates is due to a similar rearrangement, we should expect salol, for example, to form 2,2'-dihydroxybenzophenone. The ultraviolet absorption curves for salol before and after exposure in cellulose acetate butyrate film, when compared with the absorption curve for 2,2'-dihydroxybenzophenone (Fig. 2), show that the latter certainly cannot be the only photoproduct. If, however, a *para* Fries rearrangement also occurs, a second photoproduct, 2,4'-dihydroxybenzophenone would be formed, as shown in eq. (2), with resulting complication of the ultraviolet absorption curve.



The absorption curve for 2,4'-dihydroxybenzophenone has been included in Figure 2, along with a curve calculated for a mixture of 40% 2,2'-dihydroxybenzophenone, 20% 2,4'-dihydroxybenzophenone, and 40% unreacted salol.

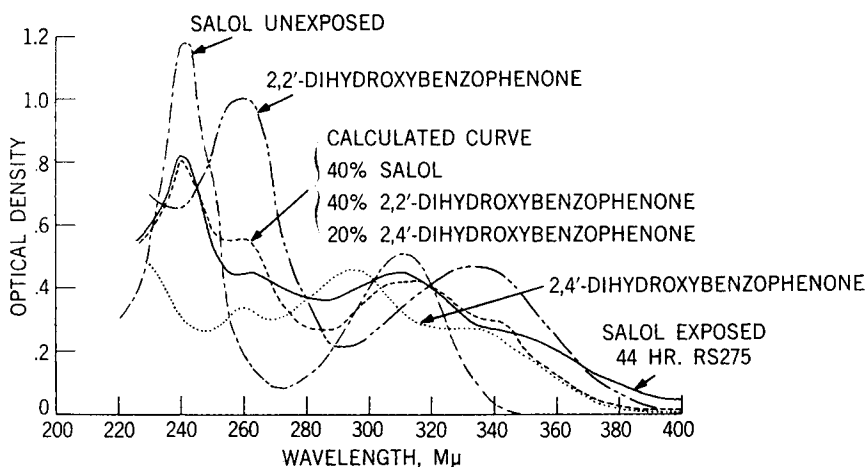


Fig. 2. Photochemical conversion of salol.

Clearly, there is a resemblance to the curve observed for exposed salol. Anderson and Reese⁴ observed a secondary isomeric photoproduct from catechol monoacetate. The case of RMB is one of fortuitous simplicity, in that either *ortho* or *para* rearrangement would result in the same product.

Results and Discussion

Low density polyethylene compositions containing aromatic salicylates were weathered outdoors at Kingsport, Tennessee, in the form of specimens 1.5 in. \times 0.5 in. cut from compression-molded plates 0.125 in. thick. The additives were mixed into the plastic on compounding rolls for 4 min., with the front roll at 270°F. and the rear roll at 220°F. These specimens were mounted under stress by bending them into a U-shape and inserting them upside down into 0.5-in.-wide aluminum channels. Ten samples of each composition were thus exposed, and the outdoor stress-crack life was taken as that exposure required to develop cracks visible with the unaided eye in 5 of the 10 samples. Table I lists the performance of several illus-

TABLE I
Stabilization of Polyethylene with Aromatic Salicylates

Salicylate ^a	Yellowing	Outdoor stress-crack life, mo.
None	None	12
Phenyl (salol)	Very slight	22
<i>p</i> -tert-Butylphenyl (TBS)	Slight	40
<i>p</i> -Biphenyl 5-phenyl	Much	49
<i>p</i> -Biphenyl	Much	72
Phenyl 3-phenyl	Some	>85
<i>o</i> -Octylphenyl	Some	>85

^a Nominal concentration 1%.

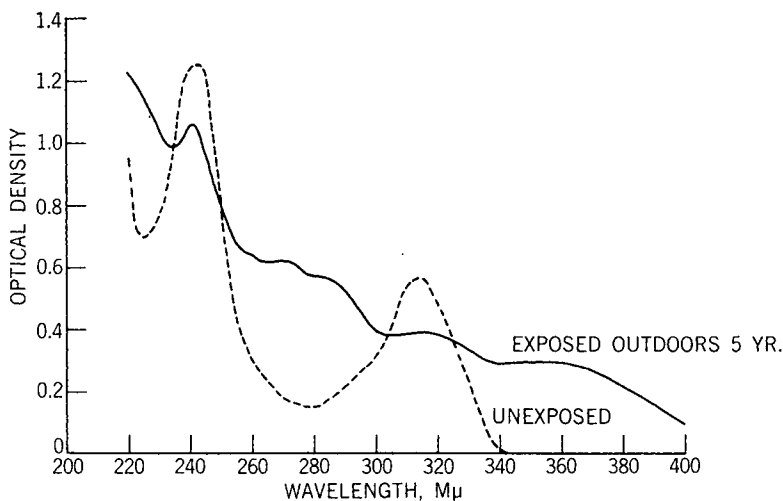


Fig. 3. Ultraviolet absorption of *o*-octylphenyl salicylate in polyethylene.

trative compositions. The increasing effectiveness of stabilization with increasing molecular weight of the salicylate is quite striking. Ultraviolet absorption curves run on the composition containing *o*-octylphenyl salicylate (Fig. 3) before and after 5 years of outdoor exposure show that the same general type of photorearrangement discussed for salol in cellulose acetate butyrate occurs in polyethylene plastic during actual weathering. In accordance with eq. (2), the photoproducts to be expected in this case would be 2,2'-dihydroxy-3-octylbenzophenone and 2',4-dihydroxy-3-octylbenzophenone. The absorption curve for the exposed polyethylene containing the salicylate shows an obvious absorption in the near-ultraviolet and extending into the visible, indicating the development of yellow color in the polyethylene. Most of the yellow color is likely due to the *ortho*-rearranged product, since it is well known that di-*o*-hydroxybenzophenones are more colored than mono-*o*-hydroxybenzophenones.

When substituents are present in both *ortho* positions of the salicylate molecule, thus making any *ortho* rearrangements impossible, it was found experimentally that no yellowing was produced on exposure to ultraviolet radiation. Even the *para* rearrangement apparently does not occur in these compounds, since the ultraviolet absorption curve shows no change during the exposure. Figure 4 illustrates this for 2,6-dimethylphenyl salicylate in polyethylene. The product to be expected from *para* rearrangement, 2',4-dihydroxy-3,5-dimethylbenzophenone, is included in Figure 4 for comparison.

A number of aromatic salicylates, of both yellowing and nonyellowing types, were evaluated as ultraviolet stabilizers in polypropylene containing a low concentration of antioxidants (0.1% butylated hydroxytoluene and 0.1% dilauryl 3,3'-thiodipropionate). The salicylates were mixed into the polypropylene in a C. W. Brabender Plastograph under a nitrogen atmos-

phere for 5 min. at 325°F. The Plastograph slab was then granulated and injection-molded into tensile specimens, 0.0625 in. thick, 2.5 in. long and 0.5 in. wide at the ends, with a neck section 1.0 in. long and 0.25 in. wide. These were bent into a U-shape, mounted upside down in stainless steel channels 0.625 in. wide, and weathered in this stressed condition in an Atlas Twin-Arc Weather-Ometer, modified by the addition of 10 Westinghouse 20-w. fluorescent sun lamps.⁶ Three samples of each composition were exposed. The Weather-Ometer stress-crack life was taken as the average exposure required for cracks visible under 3× magnification to develop in the samples. Table II illustrates the range of stabilizing behavior obtainable with aromatic salicylates in polypropylene.

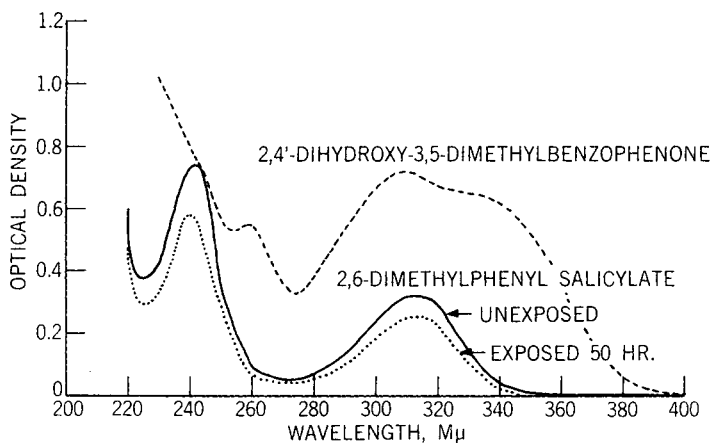


Fig. 4. Irradiated polyethylene containing 2,6-dimethylphenyl salicylate.

The yellowing observed on exposure is clearly related to the possibility of formation of 2,2'-dihydroxybenzophenone derivatives. The color of these derivatives is generally intensified by the presence of alkyl groups in the 5-position. Thus, *p*-octylphenyl salicylate and 2-dodecyl-4-methylphenyl salicylate show intermediate yellowing, and *p*-octylphenyl 5-octyl salicylate, which gives rise to a benzophenone containing two 5-alkyl groups, shows the most yellowing. The very slight yellowing developed by phenyl salicylate could be due to at least two causes. First, its relatively low molecular weight resulted in substantial loss by vaporization during compounding. By ultraviolet transmission measurements it was shown that only 0.39% of salol, instead of the nominal 1%, actually remained in the plastic composition after compounding. Second, according to Figure 2, only 40% of this residuum is rearranged to 2,2'-dihydroxybenzophenone in the exposed plastic.

Loss of stabilizers from plastics, both during compounding and subsequent exposure testing, complicates their evaluation. The losses occurring during the Brabender Plastograph compounding of a number of aromatic salicylates in polypropylene is shown in Figure 5.

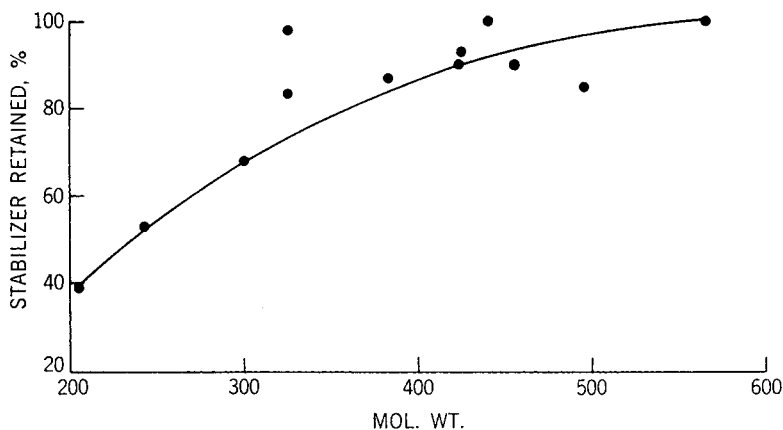


Fig. 5. Loss of aromatic salicylates from polypropylene by volatilization during compounding.

Photorearrangement with resultant yellowing is obviously not a prerequisite for stabilizing efficiency in the aromatic salicylates. For example,

TABLE II
Stabilization of Polypropylene with Aromatic Salicylates

Salicylate ^a	Major rearranged product (hypothetical)	Weather- Ometer stress- crack life, hr.	Yellowing
None	None	90	None
Phenyl (salol)	2,2'-Dihydroxybenzophenone	130	Very slight
Phenyl 3-phenyl	2,2'-Dihydroxy-3-phenylbenzo- phenone	140	Some
2-Dodecyl-4-methyl- phenyl	2,2'-Dihydroxy-3-dodecyl-5- methylbenzophenone ^b	280	Much
<i>o</i> -Octylphenyl	2,2'-Dihydroxy-3-octylbenzo- phenone	525	Some
2,6-Dimethylphenyl 5- <i>tert</i> - butyl	None	420	None
2,6-Dimethylphenyl 4- dodecyloxy	None	460	None
<i>p-tert</i> -Butylphenyl 4- dodecyloxy	2,2'-Dihydroxy-4-dodecyloxy-5'- <i>tert</i> -butylbenzophenone ^b	470	Some
2,6-Dimethylphenyl	None	500	None
2,6-Dimethyl-4-octadecyl- phenyl	None	550	None
<i>p</i> -Octylphenyl (OPS)	2,2'-Dihydroxy-5-octylbenzo- phenone ^b	1200	Much
<i>p</i> -Octylphenyl 5-octyl-	2,2'-Dihydroxy-5,5'-dioctyl- benzophenone ^b	1660	Very much

^a Nominal concentration 1%.

^b Only product considered possible.

as shown in Table II, 2,6-dimethylphenyl salicylate fairly successfully inhibited Weather-Ometer stress cracking without yellowing or rearranging. However, none of the nonyellowing salicylates have equaled the effectiveness of the better yellowing varieties, such as OPS.

In the 2-hydroxybenzophenone family of ultraviolet stabilizers, it has been found⁷ that a useful index of effectiveness is the chemical shift of the *o*-hydroxy proton in the nuclear magnetic resonance (NMR) spectrum of the 2-hydroxybenzophenone derivative. It might be expected that the NMR chemical shifts observed for the *o*-hydroxy protons in the nonyellowing, that is, assumed nonrearranging, salicylates would likewise be a

TABLE III
Stabilizing Efficiencies of the Nonrearranging Salicylates in Polypropylene

Stabilizer ^a	NMR Hydroxy chemical shift, cps.	Stabilizing effectiveness as Weather- Ometer stress- crack life, hr.
2,6-Dimethylphenyl 5- <i>tert</i> -butylsalicylate	-204	415
2,6-Dimethylphenyl 4-dodecyloxysalicylate	-227	460
2,6-Dimethylphenyl salicylate	-213	500
2,6-Dimethyl-4-octadecylphenyl salicylate	-208	550
2,2'-Dihydroxybenzophenone	-222	330

^a Nominal concentration 1%.

measure of their efficiencies as ultraviolet stabilizers. As Table III shows, the hydroxy chemical shifts for the four nonrearranging salicylates of Table II are rather closely bunched together. So, too, are the stabilizing efficiencies. The latter values are not far from those to be expected by comparison with the values found for the 2-hydroxybenzophenone stabilizers of comparable efficiency, one of which has been included in Table III for comparison.

Summary

The yellowness developed on ultraviolet exposure of plastics stabilized with conventional aromatic salicylates is postulated to be due to a photo-induced Fries rearrangement. The principal product, a 2,2'-dihydroxybenzophenone derivative, is the active ultraviolet stabilizer. Certain salicylates having substituents which prevent this rearrangement were found to be nonyellowing and moderately effective stabilizers for polypropylene.

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Résumé

De nombreux dérivés du salicylate de phényle deviennent jaunes lorsqu' ils sont exposés en solution, à la lumière ultraviolette. Ceci limite leur utilité en tant que stabilisateurs ultraviolets pour plastiques. On présente des évidences étayant la superposition qui dit que le jaunissement est dû à la formation par réarrangement photochimique *ortho* des dérivés de la 2,2'-dihydroxybenzophénone. Des salicylates aromatiques tels que les salicylates de 2,6-dialcoylphényle, dans lesquels le réarrangement *ortho* est interdit, s'avèrent être des stabilisateurs non-jaunissants quoique moins efficaces que les variétés jaunissant le mieux comme le salicylate de *p*-actylphényle. La perte du stabilisateur par volatilisation, soit au cours de la fabrication soit d'une exposition subséquente apparaît comme un facteur important dans la limitation des possibilités d'action du stabilisateur.

Zusammenfassung

Viele Phenylsalicylatderivate werden in Lösung bei Einwirkung von ultraviolettem Licht gelb. Dadurch wird ihre Brauchbarkeit als Ultravioletstabilisatoren für plastische Massen eingeschränkt. Es werden Belege für die Annahme angeführt, dass die Gelbfärbung durch die Bildung eines 2,2'-Dihydroxybenzophenonderivates über eine photochemische *ortho*-Umwandlung bedingt ist. Aromatische Salicylate wie 2,6-Dialkylphenylsalicylat, bei welchen die *ortho*-Umwandlung blockiert ist, erweisen sich als nicht gelb werdende Stabilisatoren, sind aber weniger wirksam als die gelb werdenden, wie *p*-Octylphenylsalicylat. Der Verlust an Stabilisator bei der Herstellung oder während der nachfolgenden Exposition beschränkt die Wirksamkeit eines Stabilisators in entscheidender Weise.

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