Considerable catalytic decomposition of *N*-alkylanilines occurs at temperatures of 360° to 440° C. and above.

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Ultraviolet Inhibitors for Cellulose Acetate-Butyrate Plastics

PHENYL HYDROXYBENZOATES, HYDROXYPHENYL BENZOATES, AND THEIR METHYL ETHERS

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Because phenyl *o*-hydroxybenzoate (salol) is an effective weathering agent for cellulose ester plastics, the isomers of this compound and their methyl ethers were studied. Ultraviolet absorption characteristics of the compounds were measured and weathering characteristics of plastics containing these compounds were determined.

Compounds which the data indicate to be most effective are *m*-hydroxyphenyl benzoate, *p*-hydroxyphenyl benzoate, phenyl *o*-hydroxybenzoate, and *o*-hydroxyphenyl benzoate. Those susceptible to quinone formation tend to become yellow on exposure. Those with methoxy substituents are less effective than the corresponding hydroxy compounds. High optical density in the ultraviolet range after irradiation seems to be an essential requirement but does not necessarily assure the material's being an effective inhibitor.

This study gives further insight into the question of why an ultraviolet inhibitor is effective. By use of the knowledge gained, it is possible to improve plastic formulations, so that longer life may be expected in outdoor applications such as certain irrigation and oil field installations and certain automotive parts.

THE outdoor use of cellulose acetate-butyrate plastics has been greatly accelerated in recent years by the development of ultraviolet inhibitors. Without inhibitors these plastics on exposure to outdoor conditions bleach, surface-craze, become brittle, and finally disintegrate (*5*). Previous work (*4*, *7*) has shown that outdoor degradation is primarily the result of photochemical action, and is easily followed by intrinsic viscosity measurements. The introduction of 1% phenyl salicylate into cellulose acetate-butyrate compositions has largely overcome many of these deficiencies. This development has allowed the use of these plastics in such applications as irrigation tubing, marquee letters, and tree guards on telephone wires.

Since the introduction of this inhibitor, a great deal of study has been carried out to determine the best possible structure which makes an organic compound suitable for use as an ultraviolet inhibitor. Generally, a good inhibitor has several basic requirements. First, and most obvious, the compound must have a high absorption capacity for the ultraviolet region of the solar spectrum (2900 to 4000 A.). The ideal inhibitor would cover this entire range without introducing color in the plastic. Secondly, the inhibitor should dispose of the absorbed energy in such a manner that the cellulose ester chains are not harmed. Thirdly, the inhibitor should have many of the desired characteristics of plasticizers. These include compatibility, permanence, water insolubility, and freedom from odor and from color forming on exposure. Finally, in getting rid of the absorbed energy the inhibitor itself should not be physically damaged.

In this paper a limited study of the effect of molecular structure on inhibiting action is reported. Compounds considered are based on modifications of phenyl salicylate (phenyl *o*-hydroxybenzoate) and resorcinol monobenzoate (*6*) (*m*-hydroxyphenyl benzoate). In each case the *o*-, *m*-, and *p*-hydroxy derivatives and their methyl ethers were tested. These compounds have been incorporated into cellulose acetate-butyrate plasticized with 12 parts of dibutyl sebacate in a concentration of 1 part per 100 parts of cellulose acetate-butyrate.

EXPERIMENTAL PROCEDURES

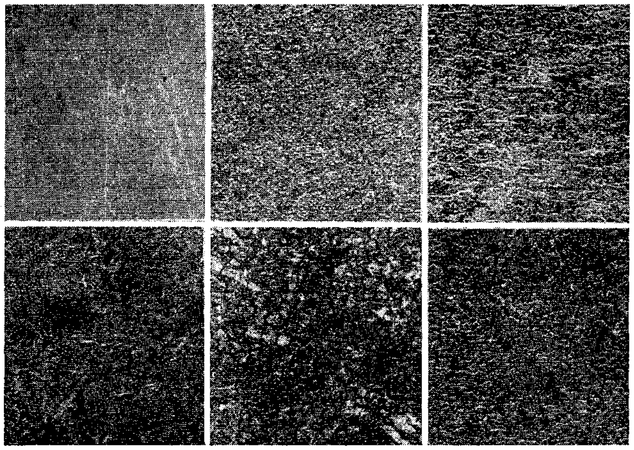
Weathering tests were made outdoors at Kingsport, Tenn.; Fort Myers Beach, Fla.; and Phoenix, Ariz. Compression-molded plastic panels, 9 × 4 × 0.125 inch, were mounted on racks at a 45° angle facing south. Sample panels were removed at periodic intervals and returned for inspection and testing. The weathered panels were first carefully examined visually, then scrubbed with soap and water and lightly flexed in order to detect first signs of checking or crazing. Finally they were cut up into test specimens and conditioned for testing. Properties determined were tensile strength, elongation, and intrinsic viscosity.

It was known from previous work that weathering breakdown began on the exposed surface of inhibited compositions and proceeded progressively inward (*5*). To get a quicker check on the progress of the surface breakdown, the intrinsic viscosity measurements were confined to the first 0.010-inch layer. These viscosities were run on a concentration of 0.25 gram per 100 ml. in acetic acid at 25° C. according to the equation: $[\eta] = \frac{\ln \eta_r}{C}$, where η_r is the relative viscosity, and C is the concentration of plastic in grams per 100 ml.

It was found necessary to run the hydroquinone monobenzoate plastics in dimethyl formamide. Fortunately, these viscosities were in the same range as the acetic acid.

In addition, the elongation and tensile strength were also determined (*2*). Results of the physical tests and observations on weathered panels are summarized in Table I.

The accelerated tests were made according to the ASTM procedure (*3*). This employs the combination of S-1 sun lamp and fog chamber, which uses 20 hours of light and 4 hours of moisture



Photomicrographs of Weathered Panels Exposed in Florida

Upper row. Resorcinol monobenzoate
Lower row. Salol
Exposed for 16, 20, and 24 months (left to right)

in each daily cycle. In this case the test was extended until the test sample failed. Failure was taken as the point of development of crazing when the 1.5 × 4 × 0.050 inch panel was flexed. In these thinner panels flex crazing was usually rapidly followed by surface crazing. Results of the tests on these inhibitors are shown in Table II.

Most of the inhibitors were synthesized in the authors' laboratory. The phenyl salicylate used was obtained commercially from the Dow Chemical Co. and used without further purification. Guaiacol benzoate was obtained from the Eastman Kodak Co. and used without further purification. The monomethyl ether of resorcinol was obtained from the Eastman Kodak Co. and reacted with benzoyl chloride by the Schotten-Bauman reaction to give the monobenzoate derivative. The other compounds were made by variations of the Schotten-Bauman reaction and were usually recrystallized several times before using. A summary of these properties and reactions is given in Table III.

Ultraviolet measurements were made with a Beckman Model DU spectrophotometer. Measurements were made on the various inhibitors dissolved in isopropyl alcohol and on the 0.050-inch strips run in the accelerated weathering test. Isopropyl alcohol was chosen because it had no interfering bands in the near ultraviolet. Infrared measurements were also taken in the near infrared region using a Beckman model.

MECHANISM OF ACTION OF ULTRAVIOLET INHIBITOR

The exact mechanism by which an inhibitor works is not known. The compound absorbs ultraviolet light and disposes of the absorbed energy in a fashion harmless to the polymer chains. Ultraviolet absorption curves show a definite shift toward the visible upon exposure to ultraviolet light (see Figures 3 to 8). Most inhibitors develop a very slight yellowing upon exposure of the inhibitor in isopropyl alcohol solution or in the plastic. This yel-

Table I. Outdoor Weathering Data

Composition, Parts	Property	Location	Blank	Months of Exposure								
				2	4	6	8	10	12	16	20	24
Cellulose acetate-butyrate (37% butyryl), 100 Dibutyl sebacate, 12 Salol, 1	Flow temperature (*1*)	Tennessee	285	282	283	281	280	281	276	275	274	276
		Arizona		282	279	281	281	274	272	279	279	..
		Florida		280	281	281	284	266	275	278	275	..
	Elongation, %	Tennessee	35	36	35	27	27	33	32	28	25	22
		Arizona		32	29	22	16	20	24	15	10	..
		Florida		32	33	32	19	22	22	18	22	..
	Tensile strength, lb./sq. inch	Tennessee	4270	4380	4460	4040	3970	4340	4600	4030	3900	3860
		Arizona		4350	4180	4040	4060	4060	3940	3980	3750	3590
		Florida		4580	4340	4300	4070	4000	3900	4125	4460	..
	Intrinsic viscosity	Tennessee	1.40	1.33	1.37	1.32	1.32	1.29	1.41	1.32	1.17	1.23
		Arizona		1.30	1.30	1.08	1.08	1.02	..	1.05	0.76	..
		Florida		1.36	1.40	1.23	1.32	1.27	1.20	1.14	1.11	1.05
Cellulose acetate-butyrate (37% butyryl), 100 Dibutyl sebacate, 12 Resorcinol monobenzoate, 1	Flow temperature (*1*)	Tennessee	286	285	283	283	279	..	..	277	276	271
		Arizona		282	281	281	285	275	274	281	264	269
		Florida		287	285	281	287	268	265	276	278	278
	Elongation, %	Tennessee	30	31	32	31	30	31	..	32	27	15
		Arizona		28	28	25	29	29	22	19	24	..
		Florida		18	15	24	4	4	28	21	34	..
	Tensile strength, lb./sq. inch	Tennessee	4150	4540	4470	4450	4130	4180	..	4250	4250	3700
		Arizona		4270	4310	4500	4450	4320	4350	3870	4140	..
		Florida		4290	3220	4000	4550	4420	4060	4210	4450	..
	Intrinsic viscosity	Tennessee	1.36	1.36	1.32	..	1.35	1.35	..	1.24	1.30	1.30
		Arizona		1.33	1.18	..	1.18	1.33	1.24	1.05	1.03	0.90
		Florida		1.34	1.27	1.20	1.16	1.29	1.27	1.09	1.15	1.03
Cellulose acetate-butyrate (37% butyryl), 100 Dibutyl sebacate, 12 *m*-Methoxyphenyl benzoate, 1	Flow temperature (*1*)	Tennessee	285	289	281	281	278	280	264	275	275	274
		Arizona		282	278	273	281	266	..	266	255	..
		Florida		282	281	282	269	265	272	273	277	275
	Elongation, %	Tennessee	40	35	36	35	26	35	31	33	23	26
		Arizona		33	26	10	14	16	13	12	4	7
		Florida		34	33	26	13	18	21	18	16	14
	Tensile strength, lb./sq. inch	Tennessee	4500	4500	3290	4330	3940	4360	4720	3980	4190	4040
		Arizona		4400	4040	4030	3940	3970	3720	3790	2700	2520
		Florida		4650	4200	3870	3830	3860	3870	3920	4440	4100
	Intrinsic viscosity	Tennessee	1.30	1.30	1.29	..	1.31	1.27	1.08	1.26	1.04	0.96
		Arizona		1.30	1.23	..	1.02	0.94	0.92	0.80	0.61	0.65
		Florida		1.23	0.94	..	..	1.06	0.87	0.87	0.86	0.97
Cellulose acetate-butyrate (37% butyryl), 100 Dibutyl sebacate, 12 Hydroquinone monobenzoate, 1	Flow temperature (*1*)	Tennessee	283	283	284	280	279	280	284			
		Arizona		285	285	285	284	285	285			
		Florida		279	279	280	285	283	285			
	Elongation, %	Tennessee	34	33	30	29	22	24	27			
		Arizona		32	28	24	18	17	8			
		Florida		34	32	28	29	24	10			
	Tensile strength, lb./sq. inch	Tennessee	4500	4540	4450	4600	4210	4230	4430			
		Arizona		4630	4450	4390	4120	4140	4000			
		Florida		4600	4670	4650	4470	4970	4120			
	Intrinsic viscosity	Tennessee	1.50	1.99	1.55	1.54	1.60	1.51	1.48			
		Arizona		1.51	1.50	..	..	1.27	1.15			
		Florida		1.56	1.52	1.58	1.61	1.50	1.61			

lowing could be caused by a breakdown or a photo-oxidation product of the inhibitor. Very little has been done to account chemically for the color changes which occur in the plastic during weathering. Inhibited cellulose acetate-butyrate plastics usually undergo some degree of yellowing which is maintained up to the time of failure. At failure the plastic will bleach rapidly, develop surface craze, and become brittle. Measurements in this laboratory have shown that the deterioration of the plastic begins at the surface and slowly penetrates deeper. At the point where the inhibitor is gradually used up and falls to a threshold concentration, the resistance to ultraviolet light is then taken up by the cellulose chains only, and rapid cleavage of these chains occurs. Loss of plasticizer and inhibitor undoubtedly occurs during outdoor exposure as the result of thermal and moisture effects. However, plasticizer recovery on weathered samples does not indicate a high degree of loss. These results were checked on Arizona samples which usually weather under very dry conditions and show very little loss. These data indicate strongly that a high degree of weathering damage is caused by photochemical effects. To date very little work has been done on careful analysis of the breakdown products.

Unquestionably, the effect of moisture, particularly by alternate wetting and drying, plays a very definite place in accelerating breakdown. Hot and humid conditions will promote growth of fungi. This is particularly true of the Florida samples. If the inhibitor used could also act as a fungicide and antioxidant, it would certainly have added value. However, as shown by oxygen-absorption measurements under accelerated conditions, the compounds considered here were not effective antioxidants and were not used in sufficient concentrations in the plastic to be effective fungicides.

Because the activity of the ultraviolet light has been shown (7) to be a source of breakdown of cellulose acetate-butyrate plastics, a study was made of the absorption characteristics of the compounds under consideration. The ultraviolet region from 2900 to 4000 A. was covered. This represents about 5% of the total solar radiation. The ultraviolet absorption spectra of benzene, phenol, benzoic acid, salicylic acid, acetyl salicylic acid, *m*-hydroxybenzoic acid, *p*-hydroxybenzoic acid, salicylaldehyde, and phenyl salicylate (salol) are shown in Figures 1 and 2. The spectral position of the wave length at which these compounds absorb their maximum energy is of interest. Thus, phenol and benzoic acid have maxima ε about 14 mμ higher than that of benzene while the increase in absorption of light energy is much greater. The greater effect of the substitution of a hydroxyl group as compared with substitution of a carboxyl group should be noted. Disubstituted groups undergo an even greater shift toward maximum absorption at longer wave length. Part of the better absorption of the salicyl derivatives may be attributed to the formation of a chelate ring which enhances absorption by being present as another resonating system. The drop in absorption maxima is shown when salol is acetylated, destroying the chelate system. This has been confirmed by outdoor tests which show that the inhibiting effectiveness of salol is destroyed upon acetylation.

Absorption data on isopropyl alcohol solutions of salol and resorcinol monobenzoate in a quartz vial before and after irradiation under the S-1 sun lamp for 24 hours are shown in Figure 3. Concentrations of the inhibitors were 0.1007 gram per 50 ml. of isopropyl alcohol. A common characteristic of these curves is that a substantial shift has occurred of the exposed sample toward a higher maximum absorption at longer wave lengths and over a wider range. The salol approaches a maximum absorption density of 1.45 at 3500 A. The resorcinol monobenzoate has a maximum absorption density of 1.7 at a wave length of 3600 A. The most interesting point is that the unexposed salol solutions started with a maximum absorption of 1.15 at 3300 A., while the resorcinol monobenzoate solution unexposed had a low absorption, reading only 0.22 at 3200 A. The exposure of the resorcinol monobenzoate brought a rapid increase after only one hour to 1.1 at 3300 A. Much the same situation exists in the accelerated test

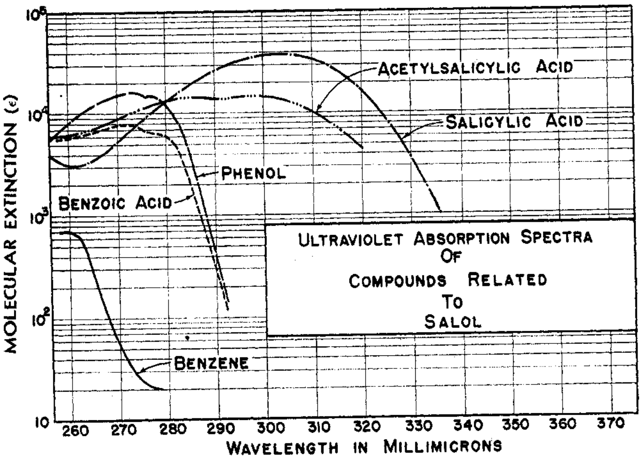


Figure 1. Ultraviolet Absorption Spectra

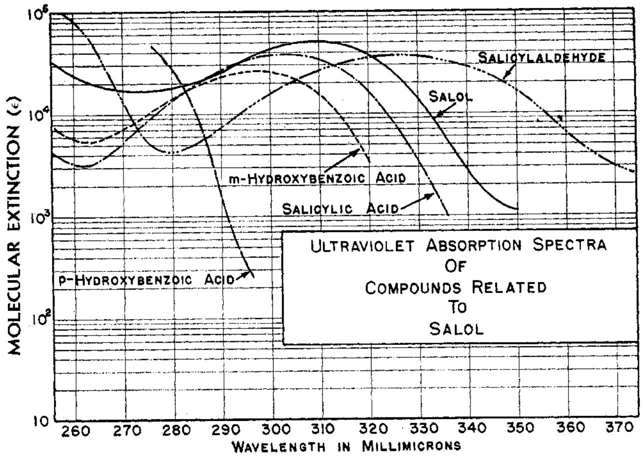
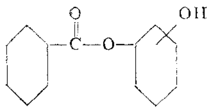
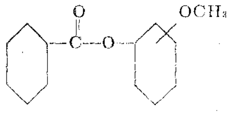
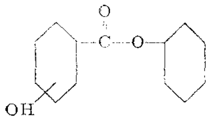
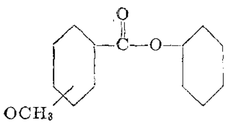


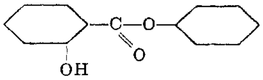
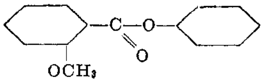
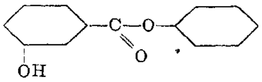
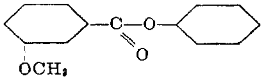
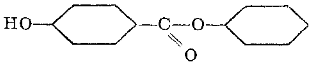
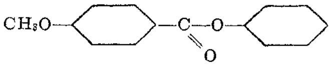
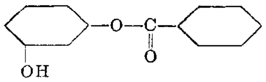
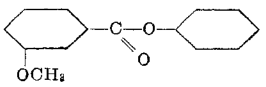
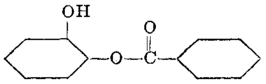
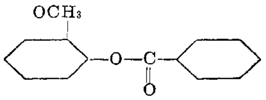
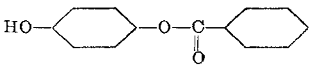
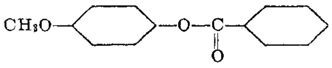
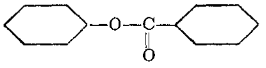
Figure 2. Ultraviolet Absorption Spectra

TABLE II. ACCELERATED WEATHERING DATA

	Hours to Failure		
	Ortho	Meta	Para
	756[a]	1400	1180[a]
	420	588	756
	800	504	420
	672	336	336

[a] Brownish yellow color formed at 50 hours' exposure. Phenyl benzoate and uninhibited blank lasted 250 hours.

Table III. Physical Data on Inhibitors

Compound	Structure	Melting Point, ° C.		% Carbon		% Hydrogen		Method of Synthesis
		Literature	Found	Theoretical	Found	Theoretical	Found	
(1) Phenyl salicylate (salol), (phenyl *o*-hydroxybenzoate)		42	41.8	72.9	73.1	4.7	5.0	Commercial grade
(2) Methyl ether of phenyl salicylate (phenyl *o*-methoxybenzoate)		59	58-60	73.7	73.7	5.3	5.6	Lab synthesis, $(CH_3)_2SO_4$ added to alkaline aqueous solution of salol
(3) Phenyl *m*-hydroxybenzoate		..	145-150	72.9	65.7	4.7	4.1	Lab synthesis, acid chloride to alkaline solution of phenol
(4) Phenyl *m*-methoxybenzoate		..	60	73.7	73.3	5.3	5.3	Lab synthesis, form *m*-methoxybenzoic acid, make acid chloride, add to alkaline solution of phenol
(5) Phenyl *p*-hydroxybenzoate		..	170-174	72.9	72.2	4.7	4.9	Lab synthesis, same as (3)
(6) Phenyl *p*-methoxybenzoate		75-76	75	73.7	73.7	5.3	5.4	Lab synthesis, same as (4)
(7) Resorcinol monobenzoate (*m*-hydroxyphenyl benzoate)		134.5	132	72.9	73.1	4.7	4.9	Lab synthesis, benzoyl chloride added to cool, dilute, alkaline solution of resorcinol
(8) Methyl ether of resorcinol monobenzoate (*m*-methoxyphenyl benzoate)		..	34	73.7	73.9	5.3	5.4	Lab synthesis, add benzoyl chloride to dilute alkaline solution of monomethyl ether of resorcinol (Eastman Kodak Co.)
(9) Catechol monobenzoate (*o*-hydroxyphenyl benzoate)		131	132	72.9	72.7	4.7	4.7	Lab synthesis, same as (7)
(10) Guaiacol monobenzoate (*o*-methoxyphenyl benzoate)		57-58	57-58	73.7	73.9	5.3	5.4	Guaiacol benzoate (Eastman Kodak Co.)
(11) Hydroquinone monobenzoate (*p*-hydroxyphenyl benzoate)		163	163	72.9	72.8	4.7	4.8	Lab synthesis, same as (7)
(12) Methyl ether of hydroquinone monobenzoate (*p*-methoxyphenyl benzoate)		87	87-88	73.7	73.3	5.3	5.3	Lab synthesis, same as (7)
(13) Phenyl benzoate		71	64-72	78.8	78.6	5.1	5.2	Lab synthesis, same as (7)

on the plastic, as shown in Figure 4. The absorption curves have been determined on the plastic before exposure and during a period just before failure. The salol plastic reaches a maximum absorption of 1.56 at 3500 A., while the resorcinol monobenzoate plastics reach 1.65 at 3600 A. The shift of the absorption curves in plastic is not so pronounced as in isopropyl alcohol. The curves of both inhibitors shift approximately the same amount. This levels out the differences noted in isopropyl alcohol solution. It is thought that the solution absorption behavior of the inhibitors is at least comparable to the absorption behavior in the plastics.

Absorption curves for isopropyl alcohol solutions of salol and its isomeric derivatives in quartz vials before and after irradiation under an S-1 sun lamp are shown in Figures 5 and 6; curves for the methyl ether of salol and phenyl benzoate are also included. All curves show good absorption characteristics in the 2900 to 3600 A. region, phenyl benzoate being the poorest. On unexposed compounds substitution of a hydroxyl group in the benzoic acid portion of the phenyl benzoates increases the absorption maximum at a slightly longer wave length. The substitution in the ortho position is the most effective in obtaining higher optical density. This may be due to the formation of a chelate ring between the adjacent hydroxyl and carboxyl groups. Methylation decreases the absorption maximum only slightly. The *m*- and *p*-hydroxy derivatives follow in that order of effectiveness. After irradiation a pronounced shift toward a higher maximum absorption at longer wave length is noted. The *p*-hydroxy substituted compound has undergone the largest increase in optical density. It is closely paralleled by the *o*-methoxy derivative, followed by the *o*- and *m*-hydroxy derivatives. These compounds shifted to the largest extent in the 2800 A. region. If the efficiency of these compounds as weathering agents is measured by the extent that they shift to higher optical densities upon irradiation in isopropyl alcohol solution, these curves would predict the most efficient weathering inhibitor to be the *p*-hydroxy derivative. The other derivatives would fall in the order: *o*-methoxy, *m*-hydroxy, and *o*-hydroxy. The latter two are similar.

Similar data on resorcinol monobenzoate and its isomeric derivatives are shown in Figures 7 and 8; *m*-methoxyphenyl benzoate and phenyl benzoate are also included in this group. In the

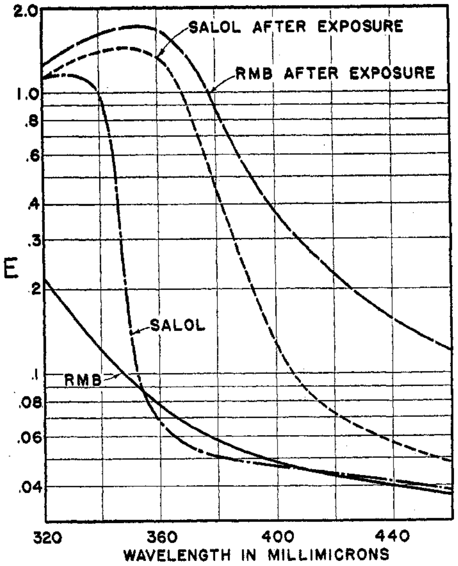


Figure 3. Optical Density Absorption Curves

Salol and resorcinol monobenzoate in isopropyl alcohol before and after irradiation

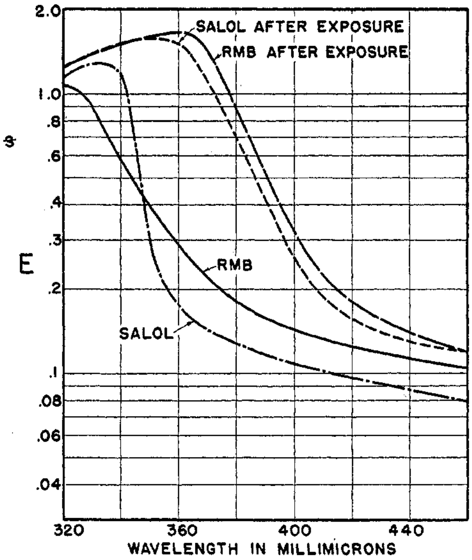


Figure 4. Optical Density Absorption Curves

Salol and resorcinol monobenzoate in isopropyl alcohol before and after irradiation

unexposed compounds the substitution of a hydroxyl in the phenyl ring of the phenyl benzoate does not appear to have as much effect as the substitution in the benzoic acid portion. The hydroxyphenyl benzoates have only slightly shifted to a longer wave length and higher absorption maximum. Irradiation, however, produces a more pronounced shift than is found with the phenylhydroxy benzoate isomers. The *m*-methoxyphenyl benzoate is slightly better than the *m*-hydroxyphenyl benzoate. Irradiation results with the catechol and hydroquinone monobenzoates are obscured by their tendency to form quinones and discolor the solution. On the basis of absorption shift upon irradiation, the most effective inhibitors should be the *m*-methoxy and hydroxy derivatives.

All of these phenyl benzoate hydroxy isomers and their methyl ethers were subjected to the sun lamp–fog chamber setup for accelerated weathering evaluation. These results are summarized in Table II. As previously noted, failure in these tests was regarded as the first signs of crazing on flexing or development of brittleness. While there is some latitude in interpreting these points and some variance in test results, this accelerated weathering procedure is a fairly reliable guide in evaluating inhibitors. As can be seen from this test, phenyl benzoate is no better than uninhibited material. The best inhibitor is resorcinol monobenzoate, which has the longest life of 1400 hours and does not de-

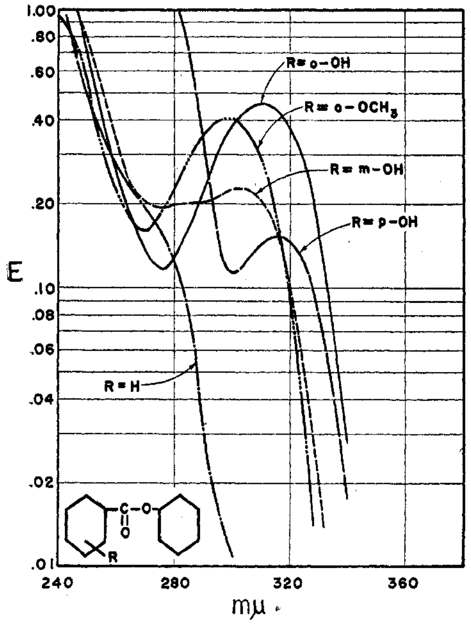


Figure 5. Optical Density Absorption Curves

R = H. Phenyl benzoate
R = OH. Phenyl *o*-, *m*-, and *p*-hydroxybenzoates
R = OCH_3. Phenyl *o*-methoxybenzoate
Before irradiation

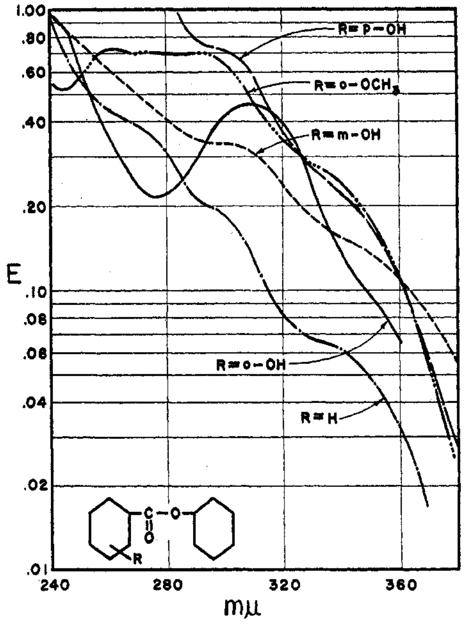


Figure 6. Optical Density Absorption Curves

After irradiation

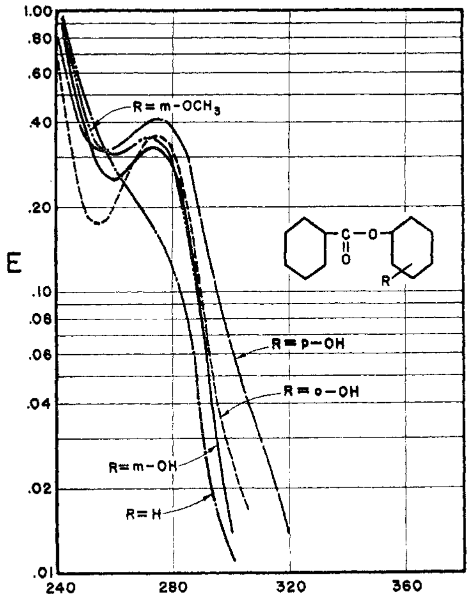


Figure 7. Optical Density Absorption Curves

Before irradiation

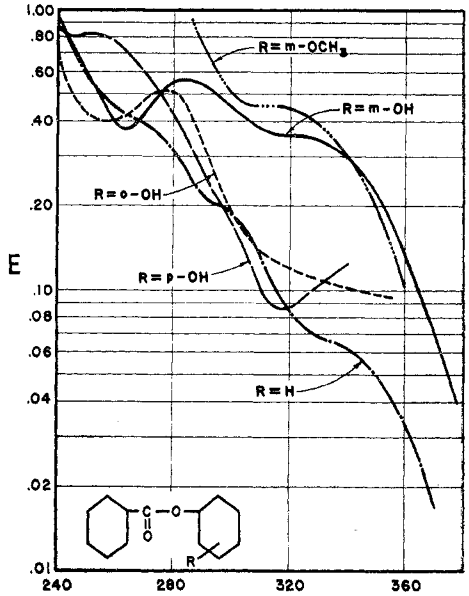


Figure 8. Optical Density Absorption Curves

After irradiation

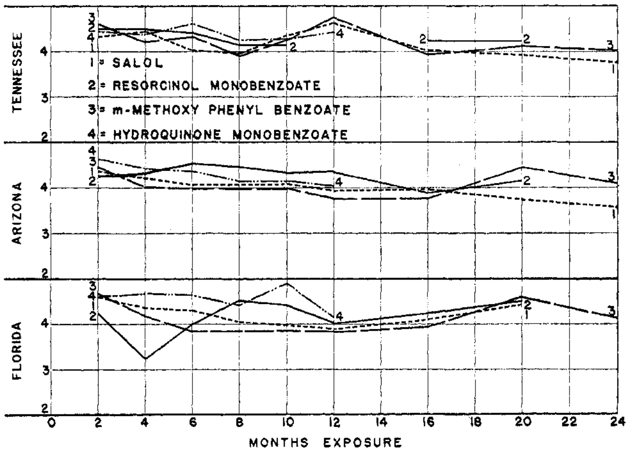


Figure 9. Intrinsic Viscosity

velop color. Its methyl ether is rather poor at 588 hours, which does not correspond with its absorption curve. The next best inhibitor is hydroquinone monobenzoate, but this could be attributed to effectiveness of the development of color in aiding the inhibiting action. Next in order come salol, catechol monobenzoate, the methyl ether of salol, and *p*-methoxyphenyl benzoate. Exclusive of color formation, the absorption curves of these compounds which undergo a considerable shift upon irradiation have possibilities as good weathering inhibitors. The poorest correlation was obtained between the absorption curve of the *m*-methoxyphenyl benzoate and its accelerated weathering performance.

Absorption curves and accelerated weathering tests in compounds may be guides to their value as inhibitors, but outdoor tests serve as the final criteria. Only four of this group of inhibitors have been exposed to outdoor conditions in Florida, Arizona, and Tennessee. These include salol, resorcinol monobenzoate, *m*-methoxyphenyl benzoate, and hydroquinone monobenzoate. Previous work (*4*) has shown that the use of an effective inhibitor as salol so reduces the breakdown of the cellulose chain that long exposures are necessary before appreciable breakdown can occur. For this reason intrinsic viscosities were determined on a 0.010-inch layer milled off the exposed surface in hope of getting an earlier indication of breakdown. Mechanical properties determined were elongation and tensile strength. Fungi growth was noted in the Florida samples. Generally, except for the color-forming hydroquinone monobenzoate, the inhibitors developed slight yellowing after one month's exposure, but this color did not increase with time. Where possible, viscosities were determined on panels exposed up to 2 years.

It was noted that the weathered hydroquinone monobenzoate plastics would not completely dissolve in acetic acid, even in the case of the sample exposed for 2 months. This may be explained on the basis of oxidation of the hydroquinone to quinone and then to polymeric quinone compounds. The color formation is typical of the hydroquinone-quinone oxidation. If this mechanism is the

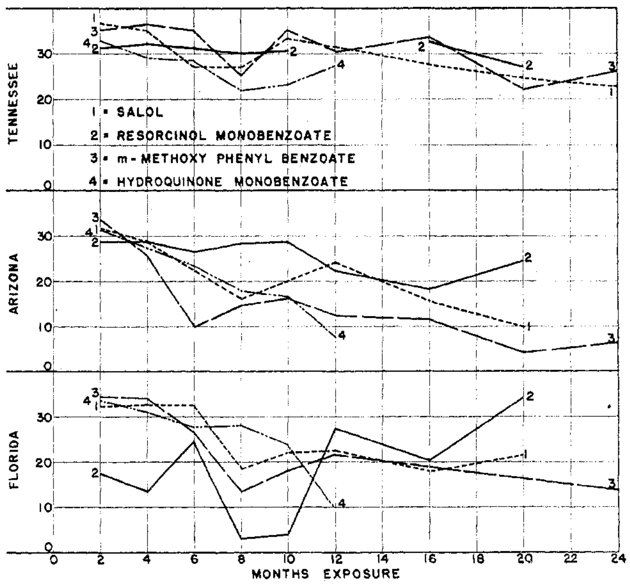


Figure 10. Tensile Strength

1×10^3 pounds per square inch

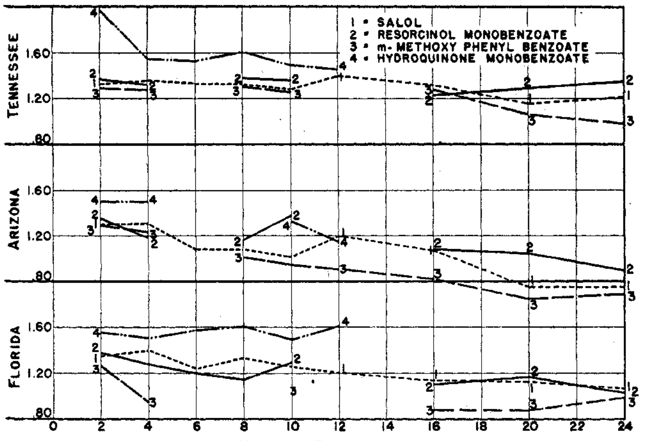


Figure 11. Per Cent Elongation

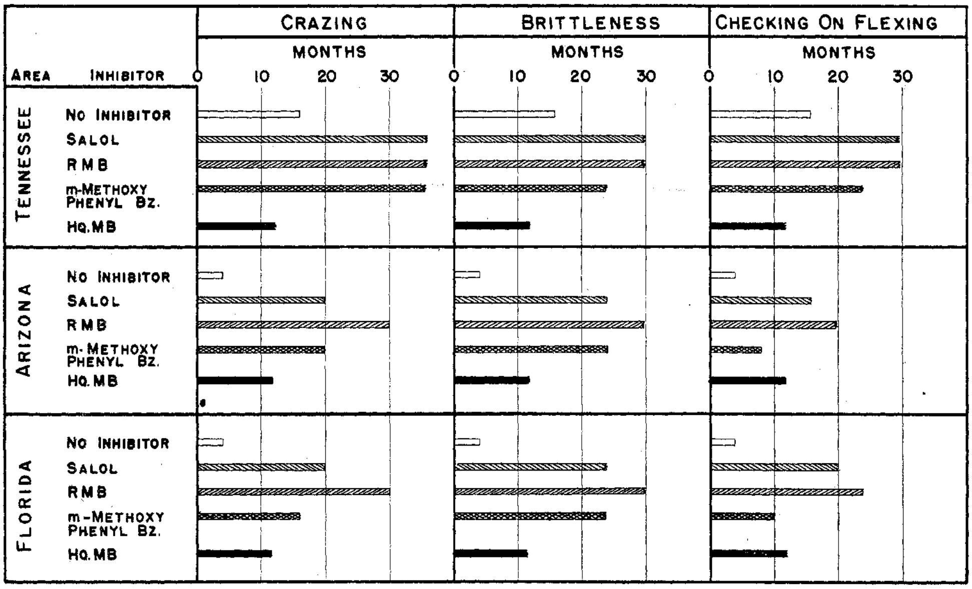


Figure 12. Outdoor Weathering Flexibility of Cellulose Acetate-Butyrate Plastics

cause of the changes, it is another example of the photochemical nature of the weathering resistance of the ultraviolet inhibitor. Quinone itself is soluble in acetic acid, but is usually rapidly converted to the polymeric form. This product apparently has value as an inhibitor, since the cellulose acetate-butyrate plastics containing the polymeric quinones were substantially unchanged at the end of one year. Intrinsic viscosities of these acetic acid-insoluble plastics were run in dimethyl formamide. These dimethyl formamide viscosities were comparable to acetic acid, but it is still possible that the polymeric quinones may have influenced the viscosities.

The viscosity of 0.010 inch of exposed layer gave the quickest indication of breakdown (Figure 9). This is especially true of samples weathered in Arizona, where the atmospheric conditions are relatively free of contaminants and not conducive to fungus growth. In Florida the hot and humid climate developed a covering of black fungus which blanked out much of the light. Local conditions in Tennessee covered the samples with a layer of cement dust and factory dirt from smoke and tar sources. The intrinsic viscosities in Arizona samples show most clearly that resorcinol monobenzoate is the best inhibitor. Salol is next, followed by the hydroquinone monobenzoate and *m*-methoxyphenyl benzoate. Measurements of mechanical properties, as elongation and ultimate tensile strength, are not as indicative, as they are sensitive to the surface imperfections developed during exposure, and they are based on the entire thickness of the plastic rather than on the surface. Tensile strengths show no significant trend (Figure 10). However, elongations of the plastic fail noticeably in the more severe climates (Figure 11). Plastics protected by resorcinol monobenzoate show only a slight drop in elongation. Salol, hydroquinone monobenzoate, and *m*-methoxyphenyl benzoate again fall in that order. Two years' exposure of the *m*-methoxyphenyl benzoate drops the elongation from 60% to only about 10%.

The visual observation of development of checking on flexing, surface crazing, and brittleness is correlated with the exposure time in Figure 12. Lines with broken ends indicate continuing tests. Various salol inhibited plastics have shown signs of checking on flexing from 12 to 20 months in Arizona. In this particular test the salol plastics first checked in 16 months, while resorcinol monobenzoate checked on flexing at 24 months. The more important property from a commercial viewpoint is the surface crazing. In Arizona or Florida salol ran for 20 to 24 months without surface crazing, while resorcinol monobenzoate lasted for 30 months. *m*-Methoxyphenyl benzoate began checking on flexing at 8 months in Arizona or Florida and began surface crazing at 20 months. Hydroquinone monobenzoate had been exposed for only 12 months and was substantially unchanged at that time. Slight checking could be detected on the Arizona sample. In the case of the Tennessee samples, surface crazing failed to show up after 36 months' exposure for resorcinol monobenzoate, 24 months for salol, and 20 months for *m*-methoxyphenyl benzoate. Usually, after the initial development of surface crazing, the test panels retained a fairly high degree of flexibility.

In the reporting of these data it should be remembered that protection is being given to the polymeric system cellulose acetate-butyrate-dibutyl sebacate. A change of base material may produce a marked change in weather resistance. A change in plasticizer can also affect the weathering resistance.

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