between the mercaptan groups of each of two molecules of lignin and thus molecules of greater size are formed. The lower viscosities of the solutions of the pyridine-soluble portions of the acetone- and methanol-insoluble fractions of the lignin would be expected. If solutions were prepared of the pyridine-insoluble materials of these fractions, their viscosities would probably be greater than that of the unchanged pine wood lignin in the same solvent.

INDICATED MOLECULAR WEIGHT OF LIGNIN MATERIALS

In a study of lignins isolated from wood by phenol and resorcinol it was noted that the specific viscosities of the chloroform solutions of these lignins at concentrations of 1% or below were directly proportional to the concentrations and that viscosity-concentration curves were linear (*6*). The specific viscosities of these solutions at the lower concentrations were 0.030 to 0.065. More detailed studies of similar lignins in acetone, acetic acid, and dioxane solutions (*5*) confirmed the earlier work. The specific viscosities of 1% solutions of phenol lignin, acetylphenol lignin, *o*-cresol lignin, acetyl-*o*-cresol lignin, beechwood lignin, and a sodium lignosulfonate in acetone and acetic acid were from 0.030 to 0.065. These values corresponded very closely to that of cellopentaose acetate, whose molecular weight was 1542. A lignin obtained by digestion of spruce wood in concentrated formic acid gave a molecular weight of 1000 by freezing point depression of dioxane. The specific viscosity of a 1% solution of the same lignin in dioxane or formic acid was 0.065 to 0.070. By using the molecular weight of the formic acid spruce lignin as 1000 and its specific viscosity of 0.065, and assuming the weight-viscosity relationship to be a straight-line function, Figure 4 was prepared. From Figure 2 specific viscosities at 1% concentration were obtained and are indicated on Figure 4. The molecular weights as indicated in Figure 4 vary from 900 to 2900.

In a study of native black spruce lignin, the viscosities of some dilute solutions of the lignin in dioxane were determined (*2*). Various fractions of the lignin having molecular weights estimated at 2800 to 5800 were studied. The reduced viscosities (specific viscosity per unit concentration) of 1 and 2% solutions varied from 0.05 to 0.10. Calculations of the reduced viscosities of the pine wood lignin-pyridine solutions from the curves of Figure 2 give values of 0.06 to 0.23. Assuming the specific viscosity-concentration relationships for the native black spruce lignin-dioxane solutions and the pine wood lignin-pyridine solutions are comparable, it appears that the two lignins are of about the same molecular weight.

The viscosities of some dilute solutions of purified (by exhaustive dialysis) sodium lignosulfonates and lignin sulfonic acids from a sulfite waste liquor have been determined (*1*). The specific viscosity–concentration relationship of these aqueous solutions was shown to be a lineal function. A plot of this viscosity-concentration relationship is shown in Figure 5, with similar plots of like values of solutions of three pine wood lignins. The two types of lignins appear to have molecular weights of the same magnitude. Estimated molecular weights of 3000 to 20,000 have been obtained for lignosulfonates from spent sulfite liquors by calculations from light-scattering measurements (*3*) and determinations of diffusion coefficients (*4*).

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Weathering of Poly(vinyl Chloride)

Effect of Composition

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Plasticized poly(vinyl chloride) (PVC) is being used in an increasing number of outdoor applications, particularly in the outside telephone plant, where it appears as extruded wire coatings, injection molded parts, and dispersion coatings on textiles. Serviceable outdoor compositions are possible through the judicious choice of stabilizers and pigments (*8*). The series of colored poly(vinyl chloride) coatings used on the two new types of outdoor telephone wire known as B Urban and B Rural Wire are practical applications of these principles (*20*). On the basis of a 4-year study in Florida, a minimum outdoor life of 10 years has been predicted by Griesser and Higgins (*15*) for properly pigmented materials.

Poly(vinyl chloride) plastics are not inherently weather-resistant and derive their properties in this respect mainly through formulation. The purpose of the present studies has been to assess the effects of weathering on various resins, plasticizers, and light absorbers. Through work of this kind, it is hoped to accumulate technical data useful in formulating outdoor compositions designed for specific applications.

The formulations reported here are not intended for any specific applications, however, and should be viewed only as vehicles in which the variables are being investigated. As the samples weathered, their attrition was followed primarily by the measurement of physical properties. Natural weathering was used exclusively, with diverse climates, to obtain the maximum possible effect.

MATERIALS

The mixing procedures were essentially those followed in the previous investigation (*8*). Compositions were mixed on hot rolls and press-molded to test sheets 0.030 inch thick, except where noted. Three series of experimental compositions were studied in which the resin, plasticizer, and organic ultraviolet absorber were varied.

Table I. Original Properties of Materials Used in Study of Poly(vinyl Chloride) Resin

Base Formulation	Parts by Wt.
Resin	100
Di-2-ethylhexyl phthalate (DOP)	65
Dibasic lead phosphite	6.5
Clay, calcined	10
Calcium carbonate	20
Titanium dioxide, Al-treated rutile[a]	3.5
Antimony trioxide	4.0
Stearic acid	0.5
Mineral oil	2.0

	Resin				Stress-Strain Properties of Base Formulation	
			Particle Description[b]			
Expt. No.	Type	Intrinsic viscosity[c]	Size, μ	Shape	Elongation, %	Tensile strength, lb./sq. inch
352-50	Vinyl chloride	1.43	3-10	Spherical[d]	360	2440
349-50	Vinyl chloride	1.24	27-83	Spherical	390	2325
354-50	Vinyl chloride	1.18	27-83	Spherical	360	2545
351-50	Vinyl chloride	1.10	10-43	Irregular	395	2195
353-50	Vinyl chloride	1.00	23-60	Spherical	365	1895
356-50	Vinyl chloride	0.90	....		305	1785
350-50	4% vinyl acetate-chloride	1.15	10-50	Irregular	395	2195
355-50	Vinyl maleate-chloride	1.13	0.7-13	Spherical	365	1925

[a] Type II, Federal Specification TT-T-425A.
[b] From microphotographs, 300 X.
[c] Cyclohexanone at 25 °C.
[d] Dispersion grade resin.

Table II. Plasticizer Series Formulations

	Parts by Weight		
	Natural	White	Black
Poly(vinyl chloride) resin[a]	100	100	100
Plasticizer	65	65	65
Basic silicate of lead	6.5	6.5	6.5
Titanium dioxide[b] (Al-, Si-, Zn-treated)	....	10	....
Channel black[c]	....	....	10
Mineral oil	2.0	2.0	2.0
Stearic acid	0.5	0.5	0.5

[a] Resin used in 349-50 (Table I).
[b] Type III, Federal Specification TT-T-425A.
[c] Average particle size of 20 mμ.

Table III. Average Weather Conditions, 1949-1955

	New York City	Miami, Fla.	Phoenix, Ariz.
Precipitation, inches	42.4	49.6	7.1
Average relative humidity	65.4	74.0	42.7
Daily solar radiation[a] (langleys)[b]	331	463	545
Temperature, °F.			
Av.	55.7	75.6	70.6
Max.	96.3	92.7	113.0
Min.	8.4	40.1	25.7

[a] Average of 4 years.
[b] 1 langley equals 1 gram-calorie per sq. cm.

Included in the resin series were six homopolymers varying in molecular weight and particle size, a 4% acetate copolymer, and a maleate copolymer. The original properties of the base resins and the experimental compositions are given in Table I. The homopolymer resins are arranged in descending order with respect to intrinsic viscosity, which approximates their molecular weight relationship.

A group of 15 reputedly primary plasticizers for poly(vinyl chloride) were investigated in natural, white, and black formulations (Table II). Some data on laboratory-accelerated aging have been presented for this series (*8*), but this is the first time that natural weathering has been reported. The materials selected included phthalates, terephthalates, phosphates, polyesters, a pentaerythritol ester, and an acrylonitrile-butadiene copolymer. The plasticizers were technical grades of commercially available materials with two exceptions. The di-2-ethylhexyl terephthalate (boiling point at 3 mm. 238–42 °C.) and the diisooctyl terephthalate (boiling point at 2 mm. 256–8 °C.) were prepared in the laboratory. The alcohol for the latter was obtained from the oxo process, which yields a mixture of octyl isomers (*12, 26*). The diiso-octyl phthalate (DIOP) used in composition 84-52 (Table IV) and the stabilized grade in 87-52 were also manufactured from oxo alcohols. The plasticizer referred to as dioctyl phthalate in 82-50 is a commercial material that appears to be a mixed ester of 2-ethylhexyl and other branched-chain alcohols (infrared analysis). A deviation from the regular formulations occurred in the case of the acrylonitrile-butadiene copolymer composition (93-54), where 90.75 parts of poly(vinyl chloride) resin were used with 74.25 parts of plasticizing copolymer introduced as a colloidal blend.

EXPERIMENTAL

Exposure racks facing south at an angle to the horizontal of 45° in New Jersey and 30° in Florida and Arizona were used. Recent information obtained by ASTM Committee D-20 on Plastics indicates, however, that no significant differences in weathering occur for exposure angles of 30° to 45° at locations within the continental United States.

An improved type of rack and panel is now used at the New Jersey site. The new racks are of welded aluminum, and sample panels can be installed quickly by simply sliding into place (Figure 1). Cleats at the top, bottom, and sides of the rack hold the panel securely. The panels are 37.5 inches long and have a rolled edge to provide the necessary rigidity between supports.

The climatological conditions that prevailed in the test areas from 1949 to 1955 (Table III) were ascertained by examination of the records of the U. S. Weather Bureau (*27, 28*). The data before averaging showed no recognizable climatic trends, but did contain periods of marked diviation from the normal. The most noticeable of these was the 71.3-inch precipitation reported in 1953 for Florida, which was 21.7 inches over the 6-year average. The total solar radiation reported was reasonably uniform from year to year at each area. Daily solar radiation figures for each location were averaged for each year of the 4-year exposure period. Variations between these annual averages were ± 8.3% for New York, ± 2.8% for Florida, and ± 2.1% for Arizona. Although these differences are small, they do not preclude the possibility of major variations in the ultraviolet, as this portion of the spectrum contributes only about 4% of the total energy recorded.

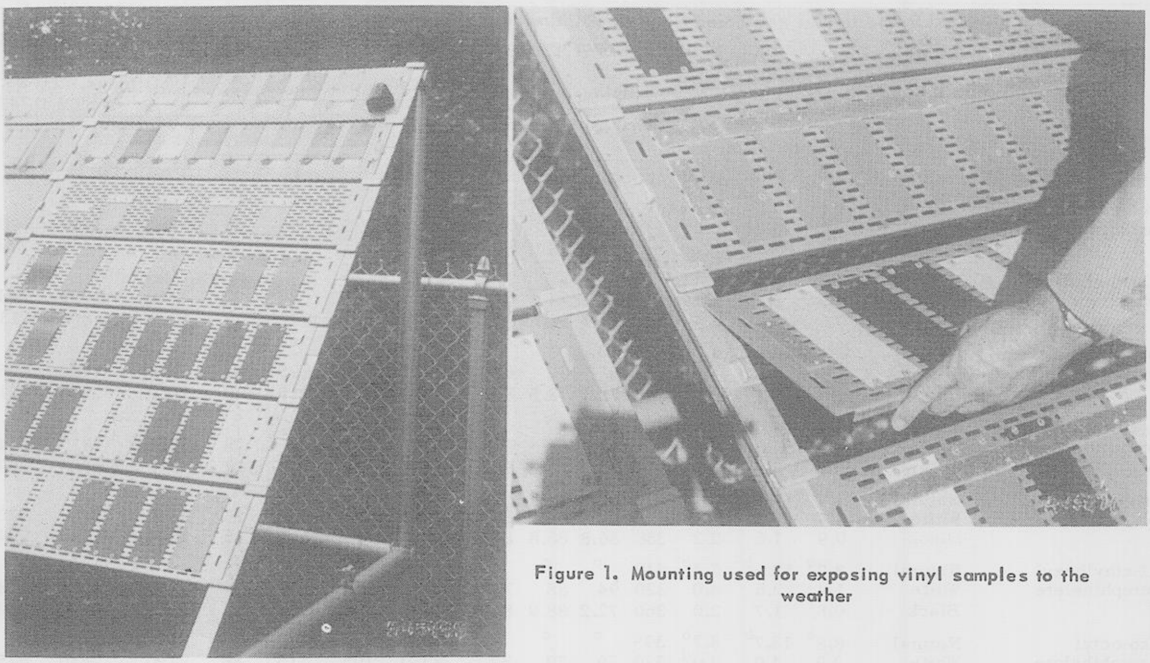

Figure 1. Mounting used for exposing vinyl samples to the weather

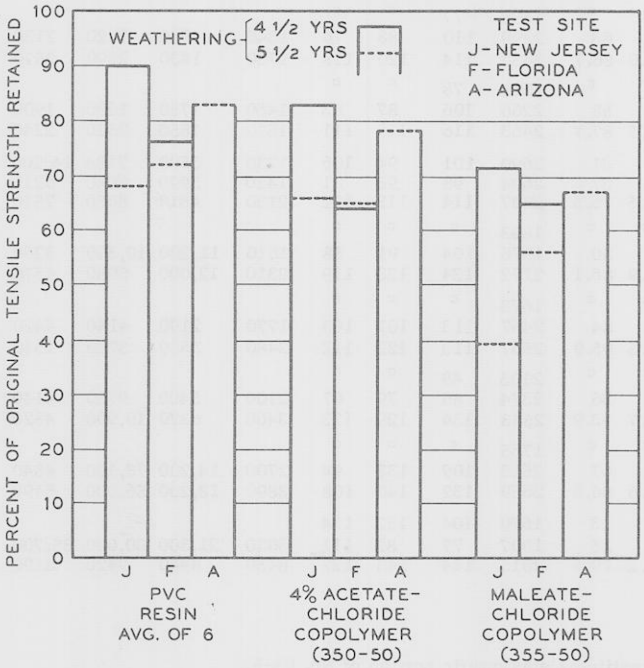

Figure 2. Retained tensile strength after weathering

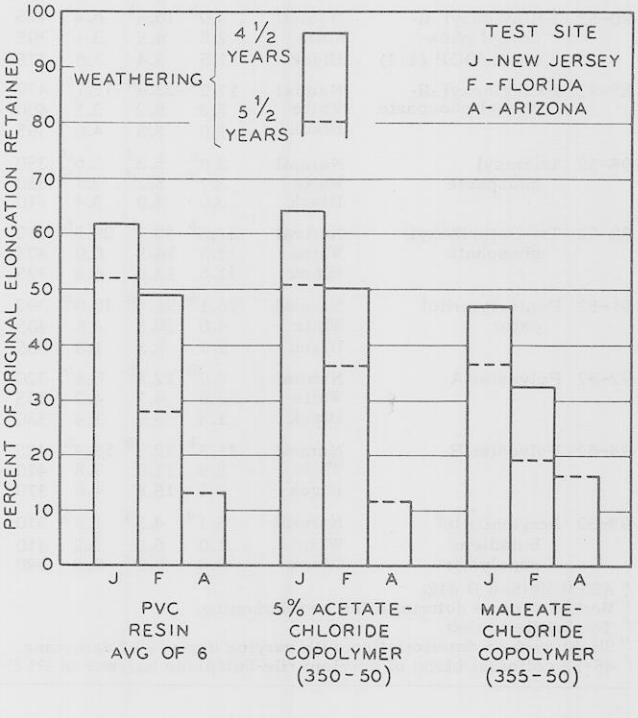

Figure 3. Retained elongation after weathering

Test Methods. Tensile Strength and Elongation. ASTM Designation D 412 using a modified *T*-50 specimen from ASTM Designation D 599 (*1*).

Stiffness. ASTM Designation D 747 (*1*).

Weight Change. Specimens 1 × 3 × 0.075 inch were weighed periodically on an analytical balance.

Light Absorption. Transmittance measurements were made on a Beckman Model B spectrophotometer using a specimen 0.0005 inch thick, supported during measurement by a frame, and results were reported as absorbance per centimeter, in agreement with suggested terminology (*18*). The light absorption coefficient previously used (*8*) may be converted to absorbance per centimeter by dividing by 5.84.

EFFECT OF RESIN VARIATIONS

At present poly(vinyl chloride) resins are offered in a range of molecular weights and particle sizes, as well as in copolymer modifications. Literature references concerning the importance of these variables are rather limited. Hendricks and White have stated (*17*) that in some cases the vinyl chloride homopolymer weathering life may be twice that of a copolymer-based plastic, which may in turn have twice the life of a paste resin, whereas random pigmented extrusion compositions based on homopolymers and low acetate (4%) copolymers did not differ significantly in earlier work at these laboratories (*8*). The results of the present investigation indicate that a truer picture of the situation may lie somewhere between these extremes.

The results of stress-strain tests on samples with 4½ and 5½ years' exposure are plotted in Figures 2 and 3.

Table IV. Physical Properties of Weathered Poly(vinyl Chloride) Compositions Containing Various Plasticizers
[43 to 48 months' outdoor exposure (1952–1956)]

Expt. No.	Plasticizer	Pigmentation	Weight Loss, %			Elongation^a				Tensile Strength^a				Stiffness, Lb./Sq. Inch, ASTM D 747			
						Orig., %	% of Orig. Retained			Orig., lb./sq. inch	% of Orig. Retained						
			N.J.	Fla.	Ariz.		N.J.	Fla.	Ariz.		N.J.	Fla.	Ariz.	Orig.	N.J.	Fla.	Ariz.
83-52	*n*-Octyl *n*-decyl phthalate	Natural	11.5^b	19.2^b	9.1^b	410	^{c}	^{c}	^{c}	1662	^{c}	^{c}	^{c}				
		White	1.5	3.2	2.6	435	83	71	64	2404	93	88	88	1480	1710	1980	1840
		Black	0.4	3.4	1.7	390	87.6	84.6	82.1	2379	123	120	115	2050	2170	2720	2110
81-52	Di-2-ethylhexyl phthalate (DOP)	Natural	9.5^b	15.2^b	9.5^b	410	4	^{c}	^{c}	2223	26	^{c}	^{c}				
		White	1.4	2.5	4.1	400	81	74	63	2341	107	84	80	1340	1710	2130	2290
		Black	0.6	1.5	2.4	365	97.3	83.6	95.9	2365	123	110	119	1770	1890	2130	2340
82-52	Dioctyl phthalate type	Natural	8.4^b	14.4^b	8.7^b	420	2	^{c}	^{c}	1722	33	^{c}	^{c}				
		White	1.2	2.8	4.2	405	85	62	67	2417	98	95	87	1070	1690	1950	1920
		Black	0.4	1.4	2.2	395	79.7	78.5	82.2	2512	111	110	110	1880	2040	2210	2240
87-52	Diiso-octyl phthalate + 0.1 bisphenol A	Natural	10.2^b	14.8^b	9.6^b	415	5	^{c}	^{c}	2251	40	^{c}	^{c}				
		White	1.8	4.0	3.5	400	84	68	53	2336	107	95	78	1420	1920	2440	3050
		Black	0.7	1.4	2.2	365	93.2	86.3	87.7	2467	114	108	108	1990	1980	2290	2230
84-52	Diiso-octyl phthalate	Natural	9.7^b	14.8^b	10.6^b	365	^{c}	^{c}	^{c}	1730	^{c}	^{c}	^{c}				
		White	2.7	5.3	6.8^d	415	67	49	31	2456	105	96	80	1620	2590	4700	7690
		Black	0.9	1.6	2.2	380	86.8	86.8	86.8	2515	119	117	116	2040	2020	2340	2470
85-52	Di-2-ethylhexyl terephthalate	Natural	8.7^b	12.5^b	7.4^b	410	^{c}	^{c}	^{c}	1605	^{c}	^{c}	^{c}				
		White	1.4	2.6	4.0	320	94	88	72	2151	117	112	113	2220	2690	2780	4490
		Black	0.8	1.7	2.0	360	72.2	88.9	88.9	2588	92.9	107	101	2990	3230	3530	2980
86-52	Diiso-octyl terephthalate	Natural	8.8^b	13.7^b	8.7^b	395	^{c}	^{c}	^{c}	2239	^{c}	^{c}	^{c}				
		White	2.2	4.9	7.0^d	380	79	70	32	2350	108	113	88	2190	2850	5150	18,000
		Black	0.8	1.9	2.1	355	90.1	94.4	98.6	2526	113	119	109	2880	3400	3480	3400
90-52	2-Ethylhexyl diphenyl phosphate/DOP (1:1)	Natural	4.9^b	16.4^b	6.4^b	415	36	^{c}	^{c}	1698	77	^{c}	^{c}				
		White	2.8	4.5	3.1	395	77	73	63	2299	110	88	76	1340	1580	1820	2130
		Black	1.5	3.4	3.6	375	90.7	84.0	86.7	2452	114	120	118	1730	1830	2390	2570
89-52	2-Ethylhexyl diphenyl phosphate	Natural	11.2^b	23.8^b	15.7^b	420	13	^{c}	^{c}	2218	78	^{c}	^{c}				
		White	5.3	8.2	3.5	400	69	68	58	2266	106	87	83	1450	1750	1690	1900
		Black	3.0	5.5	4.0	365	83.6	79.5	87.7	2463	116	115	111	1510	1850	2310	2240
95-52	Tricresyl phosphate	Natural	2.8^d	5.3^d	3.6^d	350	57	44	31	2690	101	94	106	1230	3590	7184	14,900
		White	3.7^d	5.7^d	3.7^b	350	67	61	37	2694	98	93	81	1410	3990	6040	6210
		Black	3.0	4.9	3.4	340	76.5	67.5	76.5	2897	114	115	122	2130	4810	8050	7510
88-52	Tri-2-ethylhexyl phosphate	Natural	33.8^b	40.1^b	29.5^b	370	^{c}	^{c}	^{c}	1893	^{c}	^{c}	^{c}				
		White	13.6	14.5	6.0	405	63	51	30	1876	104	91	58	1610	11,200	10,300	3260
		Black	11.6	13.9	6.4	395	91.1	70.9	86.1	2172	134	123	119	2310	12,000	5980	4570
91-52	Pentaerythritol ester	Natural	16.1^b	21.4^b	18.0^b	395	^{c}	^{c}	^{c}	1678	^{c}	^{c}	^{c}				
		White	4.0	10.3	4.6	405	89	68	84	2457	113	101	100	1770	2190	4140	4420
		Black	2.7	8.3	1.8	365	91.8	84.5	95.9	2567	113	122	112	2480	3580	3720	2540
92-52	Polyester A	Natural	7.2^b	12.1^b	6.8^b	320	22	^{c}	^{c}	2103	48	^{c}	^{c}				
		White	2.0	4.2	4.2	365	58	41	36	2374	86	79	67	2100	5400	9780	4140
		Black	1.4	3.9	1.4	330	93.9	66.7	93.9	2543	134	129	123	3460	6370	19,900	4320
94-52	Polyester B	Natural	15.5^b	22.2^b	15.4^b	425	^{c}	^{c}	^{c}	1765	^{c}	^{c}	^{c}				
		White	8.9	11.0	7.8	420	61	12	67	2513	109	133	94	2700	14,200	78,100	4840
		Black	8.1	15.8	4.6	370	79.7	17.6	86.5	2659	132	140	108	3890	18,200	56,000	5490
93-52	Acrylonitrile^e butadiene copolymer	Natural	5.1^d	4.3^d	2.9^b	310	15	8	13	1670	104	132	134				
		White	1.0	6.8	2.2	410	20	11	15	1907	77	82	111	5010	21,300	30,000	35,700
		Black	0.0	0.0	0.3	390	79.5	78.2	79.5	2015	144	143	127	8450	8940	9420	8190

[a] ASTM Method D 412.
[b] Marked surface deterioriation and darkening.
[c] Too brittle to test.
[d] Slight surface deterioriation with varying degrees of darkening.
[e] 45–55 colloidal blend of acrylonitrile-butadiene polymer in PVC resin constitutes elastomeric portion of No. 93–52.

As the differences observed among the various homopolymers were small and random in nature, it was decided to treat them collectively. The standard deviations of retained tensile and elongation values were 8.3 and 4.8%, respectively, at any one inspection. In general, the same order of weathering was found at the New Jersey and Florida test sites. Comparison of the elongation of the Arizona samples was of little significance because of their advanced degradation. The resistance of the various resins to degradation may best be judged from the per cent retained tensile strengths given in Figure 2. Tensile strength is directly related to molecular weight, and a loss in this property may be taken as indication of a reduction in chain length. By this criterion, the homopolymers weathered best, followed by the acetate and maleate copolymers.

The mechanism of poly(vinyl chloride) degradation by weathering is believed to involve an initial dehydrochlorination process along the polymer chain, followed by formation of conjugated double-bond systems and subsequent oxidation leading to chain scission. Irradiation by a mercury arc in the presence of oxygen has been shown by Kenyon (*23*) to cause a decrease in the molecular weight, which is indicative of chain scission. Oxygen appears to be a necessary part of this reaction, for when the experiment is carried out in nitrogen or a vacuum, the molecular weight increases, indicating cross linking. In an experiment reported by Haven (*24*) some cross linking was found following exposure to the carbon arc of a Fade-Ometer. The authors' solubility studies on actual weathered samples agree best with the observations of Kenyon; no evidence of insolubility was observed in a variety of samples after prolonged aging (*8*).

EFFECT OF PLASTICIZERS

The weatherability of a plasticizer in poly(vinyl chloride) depends upon a number of interrelated variables: inherent chemical and physical permanence of the plasticizer, the stabilizers, pigments, and other compositional ingredients with which it may be associated, and the climate to which it is exposed. With plasticizers of poor oxidation resistance—for example, ether-ester plasticizers—stiffening occurs rapidly on outdoor exposure (*17*). With more oxidation-resistant plasticizers, such as dioctyl phthalate or blends of this plasticizer with dioctyl adipate or azelate, good weatherability is reported (*16*). In the present investigation, the effect on plasticizers of varying pigmentation and climate was studied while stabilization was held constant.

A primary plasticizer has been defined as one which is an active solvent for the resin and does not exude after frequent flexing or long standing (*9*). Although all the plasticizers were reported to be primary, several showed spewing on normal room storage. Some slight spewing was noticed for both of the terephthalate plasticizers (85-52, 86-52), and Polyester B in 94-52 spewed badly. The poor results obtained with Polyester B on weathering may be due largely to this incompatibility.

The physical properties obtained on the various samples after 43 to 48 months of natural weathering are presented in Table IV. Condensed graphical summaries of these data are shown in Figures 4 and 5. The per cent annual loss in weight shown in Figure 4 is an average value based on the total loss for the entire 4 years of the test. In Figure 5 the minimum retained elongation, maximum change in stiffness at any of the three test sites, and average tensile strength for all sites were selected as the most useful figures.

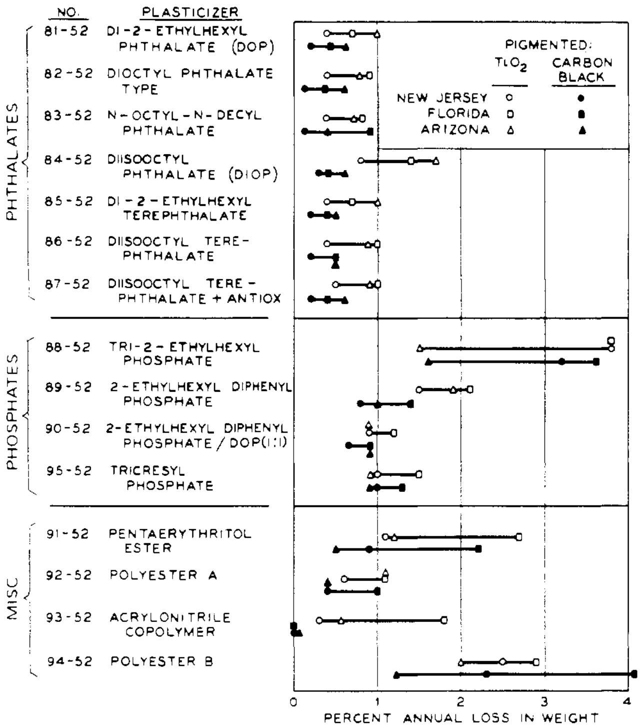

Figure 4. Effect of plasticizer on weight loss after weathering

General Observations. The results of this study emphasize the care that must be exercised in selecting a plasticizer for outdoor use. Almost without exception, the natural compositions darkened and embrittled rapidly with weathering. The need for some form of shielding against sunlight is definitely indicated for all plasticizers studied. Carbon black was universally effective for this purpose; titanium dioxide was effective in specific cases. Performance was also dependent upon climate, most plasticizers degrading more rapidly in Florida and Arizona than in New Jersey.

In most cases, the change in weight of the various samples with weathering varied inversely with the retention of mechanical properties. Exceptions were noted, however, in the case of white samples plasticized with tricresyl phosphate, Polyester A, and the acrylonitrile-butadiene copolymer. Weight losses were low in each case, so that little plasticizer could have escaped, yet retention of properties was poor in contrast with the blacks.

The effect of a moist climate on the weatherability of plasticizers is illustrated by the difference in weight loss between the Florida and Arizona samples given in Table V. Florida losses are in a number of instances higher than those observed in Arizona. The presence of moisture during weathering has been shown by Bjorksten and Lappala (*5*) to have a profound deteriorating influence on vinyl plastics, when the use conditions entail moisture or contact with an aqueous liquid.

Table V. Effect of Climate on Loss in Weight of Black Poly(vinyl Chloride) Compositions Containing Various Plasticizers

Expt. No.[a]	Annual Loss, % Arizona	 Florida	 Florida/ Arizona	Water Extraction,[b] %
Phthalates				
83-52	0.4	0.9	2.25	0.3
81-52	0.6	0.4	0.67	< 0.1
82-52	0.6	0.4	0.67	
87-52	0.6	0.4	0.67	
84-52	0.6	0.4	0.67	
Terephthalates				
85-52	0.5	0.4	0.80	
86-52	0.5	0.5	1.00	
Phosphates				
90-52	0.9	0.9	1.00	
89-52	1.0	1.4	1.40	0.2
95-52	0.9	1.3	1.45	0.7
88-52	1.6	3.6	2.25	0.6
Misc. group				
91-52	0.5	2.2	4.40	3.4
92-52	0.4	1.0	2.50	1.0
94-52	1.2	4.1	3.42	
93-52	0.1	0.0	....	

[a] See Table IV for plasticizer identification.
[b] Data from literature (*10*).

Carbon black samples were chosen for this comparison because the black pigment largely eliminates the photocatalytic effect of sunlight, leaving heat and rainfull as the prime remaining factors. Because of the higher temperatures developed by black surfaces as a result of solar absorption, thermal degradation should be accelerated in these specimens. If the phthalates are used as a guide with respect to thermal effects, exposure in Arizona is at least equal to or more rigorous than in Florida. Hence, where the Florida-Arizona ratio is greater than unity, the difference in loss is presumably due to the difference in rainfall or humidity between the two areas, resulting in leaching, hydrolysis, or biological attack. Water extraction values from the literature (*10*) help to support this line of reasoning. In Florida, the less volatile *n*-octyl *n*-decyl phthalate shows a somewhat greater loss than the di-2-ethylhexyl ester, which can probably be ascribed in part to its somewhat higher extractability. The tri-2-ethylhexyl phosphate (88-52), the pentaerythritol ester (91-52), and polyester B (94-52) were particularly affected by the Florida climate.

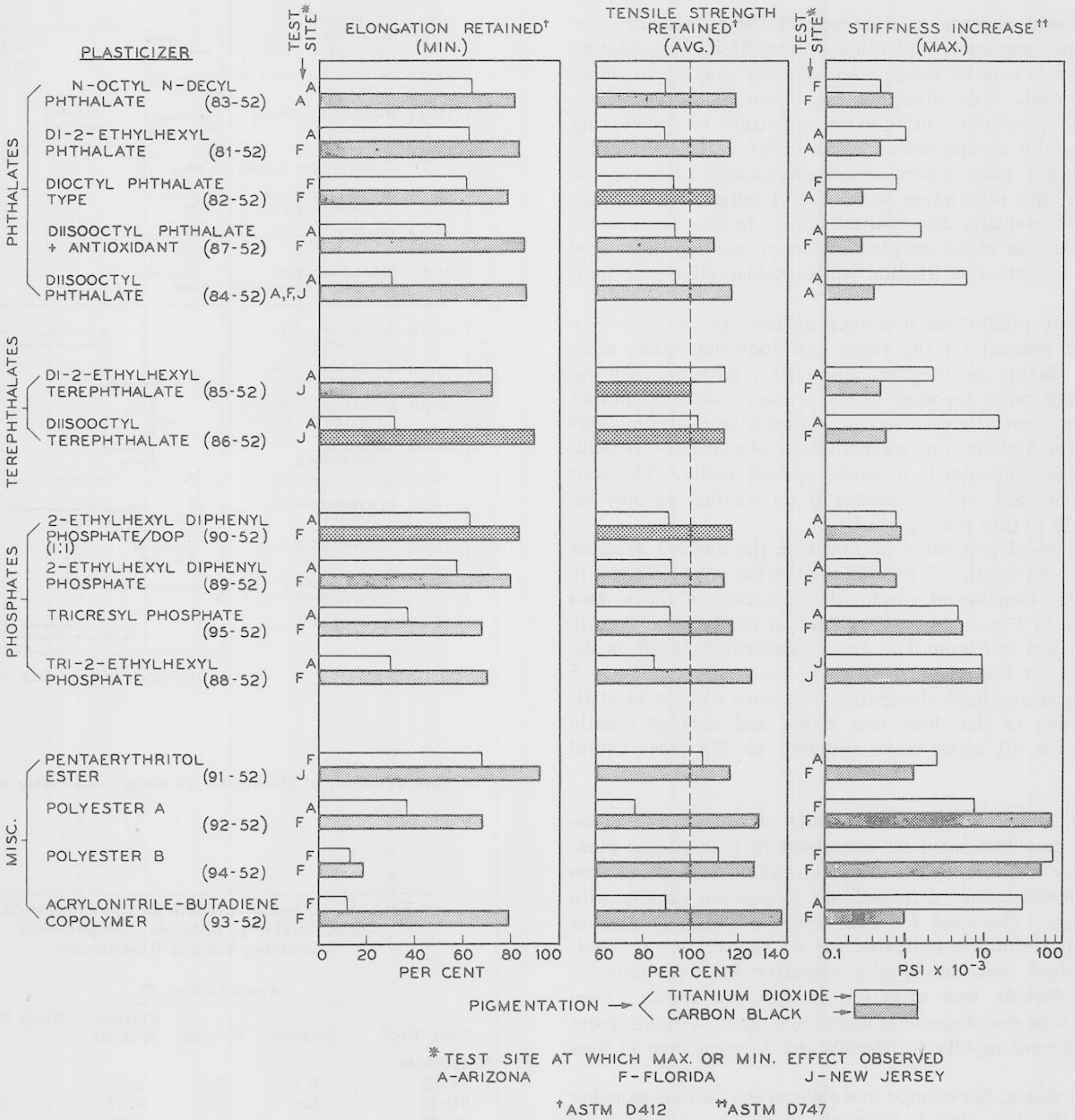

Figure 5. Effect of plasticizer on physical properties after weathering

Phthalates and Terephthalates. Plasticizers in these groups were characterized by the similarity of their resistance to weathering. The terephthalates did not show any particular advantage over the phthalates and are originally less efficient plasticizers. The superiority in heat and light resistance found by Smith, Newberg, and Young (*26*) for terephthalates over corresponding phthalate esters of isomeric alcohols does not appear to carry over to natural weathering. All the plasticizers in each of these groups gave good results when pigmented with carbon black, which points toward photooxidation as the main cause of deterioration. The di-2-ethylhexyl phthalate composition (81–52) weathered about as well as any in these groups.

The principal difference noted was in the performance of the iso-octyl esters pigmented with titanium dioxide. The diiso-octyl phthalate and terephthalate compositions (84–52, 86–52) showed poorer retention of mechanical properties than the corresponding compositions plasticized with esters of less branched alcohols. A diiso-octyl phthalate stabilized with Bisphenol A (87–52) weathered better than the unstabilized material. The use of Bisphenol A [2,2-di-(*p*-hydroxyphenyl)-propane] for stabilizing iso-octyl esters was originally proposed by Fisher, Knoth, and Newberg (*12*). Its effectiveness against thermal oxidation is shown in Figure 6; these data were obtained by a procedure described by Biggs and Hawkins (*4*). Diphenylolethyl benzene has also been shown to be an effective antioxidant for these esters (*15*).

Phosphates. The 2-ethylhexyl diphenyl phosphate alone and in combination with di-2-ethylhexyl phthalate showed the best weathering characteristics of any phosphates. Compositions containing this plasticizer showed less erosion and crazing than those containing only phthalate or the pentaerythritol ester. Although the over-all surface appearance of samples containing the phosphate was unusually good, highly localized points of degradation were observed. Occasional clusters of small pits with cracking at the base were noticed in the Arizona samples. An example of these pits magnified 10 times is shown in Figure 7, with a number of other samples.

The tricresyl and tri-2-ethylhexyl phosphate samples (95–52, 88–52) stiffened undesirably as a result of weathering. In the case of the tri-2-ethylhexyl phosphate, this is probably due to loss of plasticizer; the increase in stiffness in the case of the tricresyl phosphate suggests that it has undergone a chemical change to a less efficient plasticizer. In the natural composition, tricresyl phosphate showed the unique property of retaining a fair amount of its original properties. The natural sample from Arizona was superior in appearance to its titanium-pigmented counterpart. The natural tricresyl sample was amber in color but intact and smooth, whereas the pigmented sample had a rough brown surface, suggesting that spewing may have occurred.

Miscellaneous Group. The acrylonitrile-butadiene copolymer pigmented with carbon black is believed to be the best of this group with respect to weathering properties. This composition compared favorably with the best of the monomerics in performance and retention of mechanical properties. In vulcanizates of a polymer of this type with poly(vinyl chloride), Emmett has shown that excellent resistance to ozone and sunlight is obtained when the resin ratio is 25% or over (*11*). Work with the uncompounded acrylonitrile-butadiene-poly(vinyl chloride) resin exposed stressed in New Jersey for 10 years has shown no evidence of ozone cracking. The lower plasticizing efficiency of the acrylonitrile-butadiene copolymer, however, may limit its usefulness for some applications.

Biological Deterioration. Fungus growth was noted on several samples exposed in New Jersey and Florida. The growth was dark gray to black in nature and occurred on both the front and back of the samples, being heaviest on the back. As might be expected, the growth under the warmer and more humid conditions of Florida was more profuse than in New Jersey. No sign of fungus was observed on any Arizona samples. Compositions containing phosphates, phthalates, and terephthalates were not particularly susceptible to fungus growth, although exceptions were noted. The following samples showed fungus growth to the degree indicated.

Expt. No.	Plasticizer	Fungus Growth
83–52	*N*-Octyl *n*-decyl phthalate	Slight
86–52	Diiso-octyl terephthalate	Slight
91–52	Pentaerythritol ester	Profuse
92–52	Polyester A	Profuse[a]
94–52	Polyester B	Profuse

[a] Principally on underside.

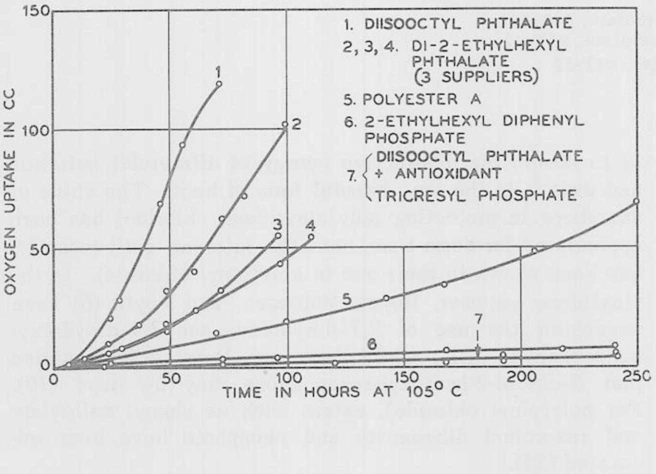

Figure 6. Thermal oxidation of plasticizers

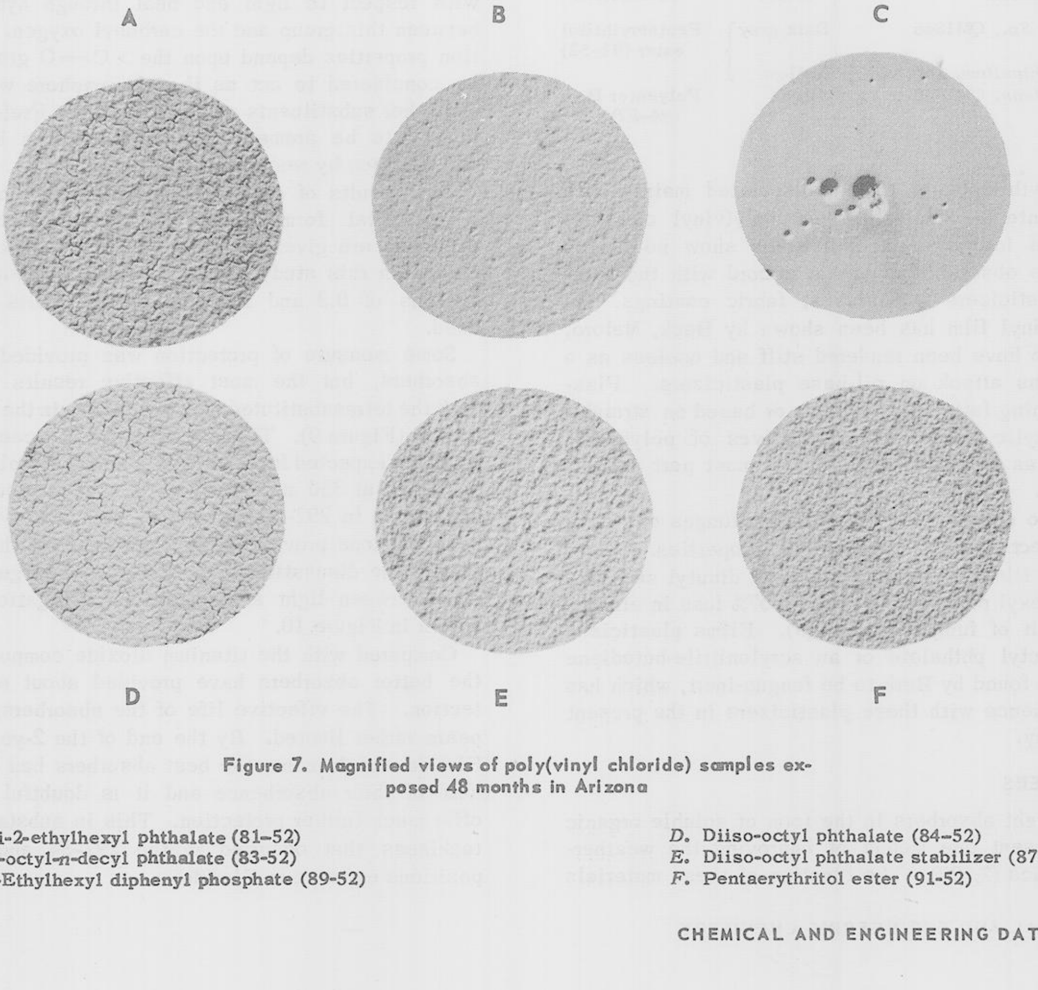

Figure 7. Magnified views of poly(vinyl chloride) samples exposed 48 months in Arizona

A. Di-2-ethylhexyl phthalate (81–52)
B. *N*-octyl-*n*-decyl phthalate (83-52)
C. 2-Ethylhexyl diphenyl phosphate (89-52)
D. Diiso-octyl phthalate (84–52)
E. Diiso-octyl phthalate stabilizer (87-52)
F. Pentaerythritol ester (91-52)

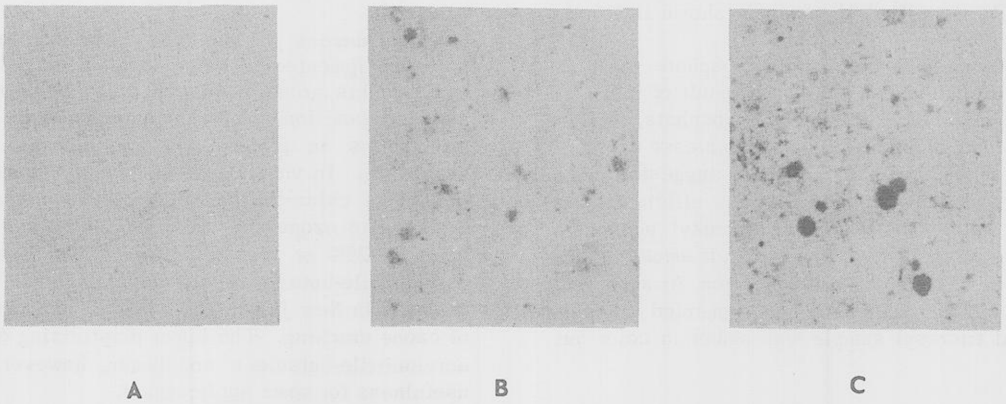

Figure 8. Effect of plasticizer on defacement by fungus

A. Di-2-ethylhexyl phthalate, 81T-52
B. *N*-Octyl-*n*-decyl phthalate, 83T-52
C. Pentaerythritol ester, 91T-52

Examples of the growth occurring in Florida on the weathered surface of 83–52 and 91–52 are shown in Figure 8. Defacement to the degree present in the pentaerythritol sample 91–52 would probably be objectionable if the color of the plastic were of importance.

Specimens of the fungus from the 91–52 and 94–52 samples that had been exposed in Florida for 2½ years were submitted to the Quartermaster Research and Development Center, Natick, Mass., for identification. The organisms given below were isolated and QM accession numbers assigned. *Pullularia* is a very common fungus and accounts for much of the defacement found on organic materials.

Organism	Color	Plasticizer
Helinthosporium Sp., QM1846	Dark gray	Pentaerythritol ester (91–52)
Penicillium janthinellum, QM1847	Yellow	
Pullularia pullulans, QM1848	Black	Polyester B (94–52)

Fungus growth appears to be associated mainly with plasticizer content. Unplasticized poly(vinyl chloride) resins exposed in the same test areas show no fungus growth. These observations are in accord with those reported for plasticizers in finishes, fabric coatings, and vinyl film. Vinyl film has been shown by Beck, Meloro, and Boor (*2*) to have been rendered stiff and useless as a result of fungus attack on oil-base plasticizers. Plasticizers containing fatty acid residues or based on straight-chain dicarboxylic acids, and derivatives of polyhydric alcohols such as pentaerythritol for the most part support growth (*13, 14*).

In addition to defacing a vinyl plastic, fungus can have a serious effect on the mechanical properties. Berk reported that a film containing a blend of dibutyl sebacate and di-2-ethylhexyl phthalate suffered a 67% loss in elongation as a result of fungus growth (*3*). Films plasticized with 100% dioctyl phthalate or an acrylonitrile-butadiene copolymer were found by Berk to be fungus-inert, which has been the experience with these plasticizers in the present weathering study.

LIGHT ABSORBERS

Ultraviolet light absorbers in the form of soluble organic additives represent one means of improving the weatherability of plastics (*7, 22*). The function of these materials is to absorb the destructive energy of ultraviolet radiation and emit it in the less harmful form of heat. The value of absorbers in protecting poly(vinylidene chloride) has been appreciated for some time, but little interest, until recently, has been shown in their use in poly(vinyl chloride). In the vinylidene polymer, Boyer, Matheson, and Moyle (*6*) have suggested the use of 2,2′-dihydroxy- and 2,4-dihydroxybenzophenone (*21*), while Jack and Horsley have stated that 5-chloro-2-hydroxybenzophenone may be used (*19*). For poly(vinyl chloride), esters such as phenyl salicylate and resorcinol dibenzoate and phosphate have been advocated (*25*).

Absorbers of this class all have hydroxy groups in the ortho position and are believed to obtain their stability with respect to light and heat through hydrogen bonding between this group and the carbonyl oxygen. Light-absorption properties depend upon the $>C{=}O$ group, which may be considered to act as the chromaphore with the —OH and other substituents as auxochromes. Preferred materials appear to be aromatic molecules with a high degree of stabilization by resonance.

The results of a 2-year weathering test on a number of experimental formulations containing substituted benzophenones are given in Table VI. Five absorbers were included in this study as well as two antioxidants; concentrations of 0.3 and 1.0 part per 100 parts of resin were used.

Some measure of protection was provided by all of the absorbers, but the most effective results were obtained with the tetrasubstituted benzophenones in the higher concentration (Figure 9). These results are in agreement with what would be expected from the light-absorption values of the compositions at 350 mμ. They show that tetrasubstituted benzophenone in 292–54 and the 2,2′-dihydroxy-4,4′-dimethoxybenzophenone provide an absorption better than three times that of the disubstituted compounds. The general relationship between light absorption and elongation retention is shown in Figure 10.

Compared with the titanium dioxide composition 304–54, the better absorbers have provided about equivalent protection. The effective life of the absorbers, however, appears rather limited. By the end of the 2-year exposure in Florida and Arizona, the best absorbers had lost more than half of their absorbence and it is doubtful if they could offer much further protection. This is substantiated by the tackiness that occurred in the 292–54 and 298–54 compositions exposed in Florida.

Table VI. Properties of Weathered Poly(vinyl Chloride) Plastics Containing Ultraviolet Absorbers and Antioxidants

(2-year outdoor exposure)

Base Plastic (272-50)	Parts by Weight
Poly(vinyl chloride) resin (PVC)	100.0
Di-2-ethylhexyl phthalate (DOP)	65.0
Basic silicate of lead	6.5
Stearic acid	0.5
Mineral oil	2.0
	174.0

Expt. No.	Ultraviolet Light Absorber	Pts. by Wt./100 Pts. Base	Absorbance per Cm. Original λ(mμ) 450	Absorbance per Cm. Original 400	Absorbance per Cm. Original 375	Absorbance per Cm. Original 350	Absorbance per Cm. Fla. 350	Absorbance per Cm. Ariz. 350	Elongation Original, %	Elongation % of Original Retained N.J.	Elongation % of Original Retained Fla.	Elongation % of Original Retained Ariz.	Tensile Strength Orig. lb./sq. inch	Tensile Strength % of Original Retained N.J.	Tensile Strength % of Original Retained Fla.	Tensile Strength % of Original Retained Ariz.
272-50	None (control)	0	84	86	92	111	...	...	350	15[a]	11[a]	24[a]	2735	32.2	47.7	30.1
289-54	2,4-Dihydroxybenzophenone	0.3	70	74	86	169	...	...	330	30[a]	60[a]	32[a]	2940	36.9	48.3	32.1
290-54	2,4-Dihydrozybenzophenone	1.0	60	63	92	282	...	...	335	42[a]	22[a]	49[a]	2985	45.1	53.6	36.3
291-54	Tetrasubstituted benzophenone mixture[b]	0.3	79	106	247	334	...	...	330	65[a]	29[a]	55[a]	3020	53.6	53.5	40.9
292-54	Tetrasubstituted benzophenone mixture[b]	1.0	96	180	633	914	361	386	315	113	98 (very tacky)	98	2840	89.3	82.6	83.1
293-54	2-Hydroxy-4,4'-dimethoxybenzophenone	0.3	98	103	135	281	...	...	340	54[a]	30[a]	47[a]	2895	49.1	59.6	42.1
295-54	2-Hydroxy-4-methoxybenzophenone	0.3	79	86	122	219	...	...	350	20[a]	50[a]	44[a]	2820	49.8	56.4	32.8
296-54	2-Hydroxy-4-methoxybenzophenone	1.0	84	89	120	253	...	...	335	67[a]	39[a]	57[a]	2820	56.0	59.2	47.3
297-54	2,2'-Dihydroxy-4,4'-dimethoxybenzophenone	0.3	77	111	279	414	...	...	335	78[a]	57[a]	73[a]	2685	74.1	70.0	57.0
298-54	2,2'-Dihydroxy-4,4'-dimethoxybenzophenone	1.0	103	187	657	842	470	461	360	99	99	107	2785	95.3	84.2	84.7
303-54	Titanium dioxide Tetrasubstituted benzophenone mixture[b]	5.8 0.3	1060	1128	1178	1229	...	...	335	94	87	93	2435	98.4	93.1	84.8
304-54	Titanium dioxide (Al-Si-Zn-treated)[c]	5.8	1266	1278	1236	1185	...	...	360	96	93	97	2460	87.7	85.7	81.5
	Antioxidant															
299-54	5-*n*-Pentadecyl resorcinol	0.3							335	24[a]	15[a]	27[a]	2830	34.6	39.2	31.8
300-54	5-*n*-Pentadecyl resorcinol	1.0							330	23[a]	11[a]	35[a]	2625	33.5	49.1	27.2
301-54	Bisphenol A	0.3							345	25[a]	16[a]	38[a]	2770	34.8	53.8	31.6
302-54	Bisphenol A	1.0							355	48[a]	24[a]	56[a]	2700	43.9	63.3	40.4

[a] Marked surface deterioration and darkening.

[b] Contains dihydroxy, dimethoxy compound along with trihydroxy and tetrahydroxy structures.

[c] Type III Federal Specification TT-T-4WA.

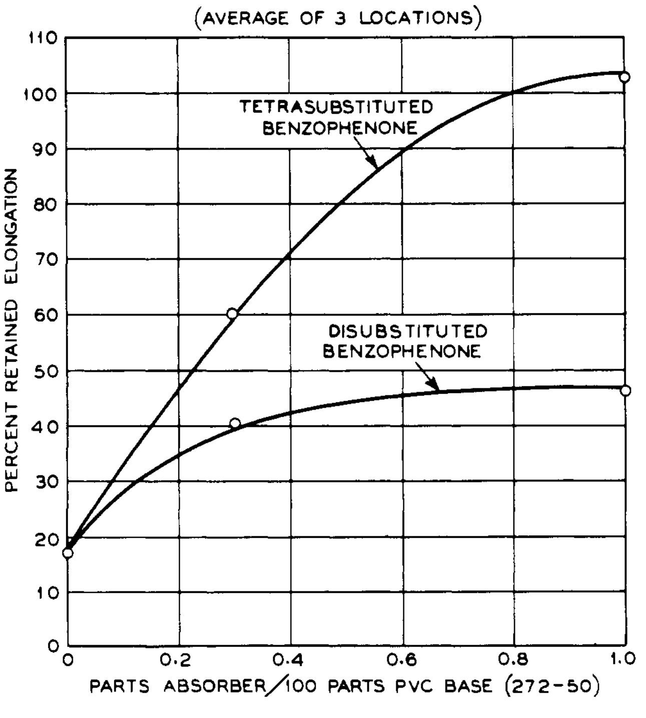

Figure 9. Effect of ultraviolet light absorbers on retained elongation after 2-year exposure (average of three locations)

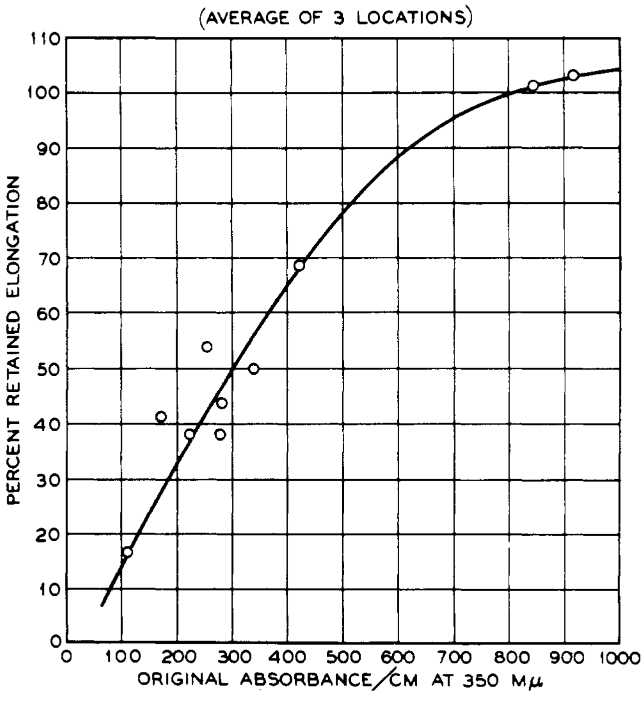

Figure 10. Relation of original ultraviolet light absorption to percent retained elongation (average of three locations), 2-year exposure

Some estimate of the wave length sensitivity of poly(vinyl chloride) can be obtained from the known transmittance characteristics of the various absorbers, which may be looked upon as filters. The disubstituted benzophenones are essentially transparent to visible light and begin to have an effective cutoff at 370 mμ, while the tetrasubstituted ones have a slight yellow color with a cutoff beginning at 390 mμ. As this polymer benefits from protection of the tetrasubstituted compounds, its sensitivity must extend into the region between 370 and 390 mμ but probably not much beyond it. In the closely related poly(vinylidene chloride), light of wave lengths below 400 mμ is credited with being almost entirely responsible for producing discoloration (*21*). In a 24-hour irradiation with a mercury arc, Kenyon (*23*), however, did not detect liberated hydrogen chloride until wave lengths shorter than 340 mμ were used. Because of its short duration, the results of this test may not be conclusive.

The antioxidants, 5-*n*-pentadecyl resorcinol and Bisphenol A, used without pigmentation, did not provide much protection. Bisphenol A in a concentration of 1.0 part was somewhat better than the control.

On the basis of these data, light absorbers and antioxidants might be expected to offer support to other forms of stabilization, such as opaque light screens, but not to be effective over extended periods as the sole protection against weathering.

CONCLUSIONS

In formulating poly(vinyl chloride) compositions for outdoor exposure, considerable freedom is permissible in the selection of a resin. Homopolymer resins varying in molecular weight and particle size show about equivalent resistance to weathering. Greater care, however, must be exercised where copolymers are concerned.

The choice of plasticizer has a marked effect, particularly in titanium dioxide pigmented compositions. The less branched phthalate and terephthalate esters show superior weathering to the more highly branched iso-octyl esters; this difference is reduced by addition of an antioxidant to the iso-octyl ester. Extractability by moisture exerts an important effect on the deterioration of compositions plasticized with tri-2-ethylhexyl phosphate and the pentaerythritol ester.

Ultraviolet light absorbers of the substituted benzophenone type improve the weather resistance of unpigmented compositions, the tetrasubstituted being more effective than disubstituted benxophenones.

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