Weathering of Plasticized Poly(vinyl Chloride)

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Synopsis

A series of flexible plasticized poly(vinyl chloride) (PVC) compositions containing different organotin compounds and ultraviolet absorbers has been exposed for 4.5 years at four outdoor sites in Australia with widely differing climatic conditions. Loss of plasticizer by evaporation during the exposure was measured and an empirical correlation was found with the average daily maximum temperature at each site. The relative effectiveness of the organotin compounds and ultraviolet absorbers in preventing deterioration of the PVC was estimated by measuring the viscosity of the polymer after exposure. This method of assessment is compared with the results of mechanical tests on the specimens.

INTRODUCTION

In order to evaluate the weathering of plasticized PVC, flexible compositions containing a number of organotin compounds and ultraviolet absorbers have been exposed outdoors at Defence Standards Laboratories, Maribyrnong, Victoria (temperate climate) and at the Joint Tropical Research Unit (JTRU) sites at Cloncurry (hot-dry), and in the "open" and in the "jungle" at Innisfail, Queensland (hot-wet). Some details of the specimens together with the results of mechanical tests conducted on specimens exposed for 1.5 years have been reported before.[1]

Extraction of the plasticizers remaining in the specimens after exposure and comparison of the climatic conditions at the respective sites should indicate whether temperature is one of the most important factors in causing loss of plasticizer.

The viscosities of the residual polymer should show which compounds have been degraded most during exposure and enable an assessment to be made of the effectiveness of the additives in preventing deterioration of the polymer itself. Comparison with the conventional mechanical properties of the specimens should illustrate the practical application of this assessment.

EXPERIMENTAL

The formulation of the PVC basic composition (P15) was as follows:

Component	Parts by weight
PVC resin	100
Dioctyl phthalate	65
Octyl-9,10-epoxy stearate	10
Calcium carbonate	10
Tribasic lead sulfate	2.5
Dibasic lead phosphite	2.0
Calcium stearate	0.5
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The PVC resin used was Corvic P55/60, supplied by Imperial Chemical Industries of Australia and New Zealand.

The additives listed in Table II were added to the compound prior to extrusion. The bronze-green pigment had the following w/w composition: synthetic iron oxide AHK/F, 11.6%; synthetic iron oxide AK/F, 5.8%; carbon black (Acarb 300), 1.2%; chromium oxide green 5E, 81.4.

The ultraviolet absorbers (S_1, S_2, Table II) and the tri-n-butyltin fumarate half-ester, Advacide N628, were used in the forms supplied by the manufacturer. The organotin compounds were prepared by standard methods.[2]

The experimental compounds used for the weatherability trials were prepared as follows. The PVC resin and all the powders, with the exception of the organotin compound, were blended in a Winkworth "Z" type internal mixer. The organotin compound was dissolved in the mixed plasticizers by heating where necessary, cooled to 60°C, and added to the dry powder blend. After blending for $1/2$ hr, the viscous plastisol was poured from the blender into a shallow tray and gelled in an air oven for $1/2$ hr at 160°C. After cooling, the PVC compound was granulated and extruded through a slit die mounted on a $1^1/8$ in. Telford-Smith screw extruder fitted with a general-purpose water-cooled screw. An air-cooled, variable-drive takeoff belt was used to produce a specimen strip 1.25 in. wide and 0.050 in. thick. The operating conditions of the extruder during the production of test strips were: screw speed, 44 rpm; filter gauze combination, 30–60–30 mesh; water outlet temperature from the screw, 25°C; power rating of the main drive, 1.9 amp; takeoff speed, 4 ft/min; rear-zone screw temperature, 155°C; front-zone screw temperature, 155°C; screw head temperature, 160°C; slit die temperature, 170°C.

Extruded samples, each 36 in. long, of each compound were exposed on racks at each site at an angle of 45°, facing north.

Standard test methods were used for the determination of tear strength,[3] tensile strength,[4] elongation at break,[4] and hardness,[5] both before and after exposure.

Standard methods were used to record the meteorologic data at the exposure sites during the period of the trial. Data are available from Defence Standards Laboratories for Maribyrnong (temperate), Innisfail (hot-

wet) in the "open" and in the "jungle," and for Cloncurry (hot-dry). Detailed long-term meteorologic data are also available.[6]

After exposure, specimens were returned to the laboratory for assessment. The plasticizers were removed by extraction using ether. A portion of the exposed strip (10 g) was cut into small pieces (0.5 × 0.5 cm) and extracted with ether (100 ml) in a Soxhlet apparatus for 8 hr. It was found that all the plasticizers in the specimen were removed in this time. The ether extract was then distilled on a steam bath, and the residue was weighed. The inherent viscosity, at 30°C, of the polymer was determined by dissolving a weighed sample of the extracted PVC compound in freshly distilled cyclohexanone (100 ml) and using the method described in ASTM D1243-66.[7] Thus, the sample (0.2 g) was transferred to a volumetric flask (100 ml), freshly distilled cyclohexanone (50 ml) was added, and the flask was heated to 85°C for $1^1/_2$ hr. The flask was then cooled to 20°C, and the solution volume was made up to the mark with cyclohexanone which had been heated exactly as the solution. An aliquot (10 ml) of the solution was decanted into a suspended-level viscometer incorporating a sintered glass filter disc,[8] the viscometer was placed in a water bath at 30°C, and after 10 min the flow time of the solution was measured. The flow time of the thermally aged cyclohexanone was measured in the same way. The inherent viscosity was then calculated as follows:

$$\text{relative viscosity} = \frac{t_1}{t_2}$$

$$\text{inherent viscosity} = \frac{\text{natural log relative viscosity}}{C}$$

where t_1 and t_2 are the measured flow times of the solution and solvent, respectively, and C is the concentration of PVC polymer in the extracted sample (g/100 ml) taken as calculated from the original formulation.

The IUPAC term for inherent viscosity is "logarithmic viscosity number."

RESULTS AND DISCUSSION

Loss of Plasticizers During Exposure

The loss of plasticizer for the control samples exposed at four different sites is given in Table I. Inasmuch as loss of plasticizer could be due primarily to evaporation, an attempt has been made to correlate this loss with typical climatic conditions at each site. Average daily maximum and average daily mean temperatures for the sites are given in Table I. A linear regression of percentage loss of plasticizer against these temperatures gave correlation coefficients of 0.994 for average daily maximum temperature and 0.987 for average daily mean temperature. The relation between loss of plasticizer and average daily maximum temperature is shown in Figure 1. This temperature would be expected to be related to the surface temperature of the PVC, and this should directly correlate with the rate of evaporation of the plasticizer.

TABLE I
Loss of Plasticizers During Exposure[a]

| Site | Loss of plasticizer, %[b] | Temperature, °F | | Total rainfall[c] | |
		Average daily maximum	Average daily mean	in.	cm
Innisfail (hot-wet)					
"open"	23.0	82.5	73.8	566.3[d]	1438
"jungle"	20.5	79.0	73.0		
Cloncurry (hot-dry)	28.2	90.7	78.2	64.3	163.3
Maribyrnong (temperate)	9.7	67.6	58.8	115.5	293.4
Calculated values for another typical site, for example, Sydney, NSW	13.6	—	63.7		
	13.0	71.1	—		

[a] Determined on control PVC compound P15 after 4.5 years of exposure. The specimens at Maribyrnong (temperate) were exposed for 5 years and the results were adjusted for an exposure period of 4.5 years.

[b] Based on the total plasticizer in the original compound.

[c] Measured over the period of the exposure trial.

[d] Measured for the "open" site; some slight differences due to the jungle canopy might be expected at the "jungle" site.

Rainfall during the trial period, as listed in Table I, which could cause loss of water-resistant plasticizer by leaching from the surface, appears to have had little or no effect. Considered independently, the very low total rainfall at Cloncurry and the very high total rainfall at Innisfail do not appear to have had any influence on the correlation between loss of plasticizer and temperature.

In hot-wet tropical areas, loss of plasticizer can occur due to attack by fungi. Dioctyl phthalate is not very susceptible to fungal attack, and loss of this plasticizer for this reason at the "jungle" and "open" sites at Innisfail is, we believe, insignificant. Other climatic factors such as wind speed and duration, relative humidity, extent of cloud cover, and sunlight intensity could have some effect on the evaporation rate of plasticizers. However, the empirical correlation found between average daily maximum temperature and loss of plasticizer, combined with the other evidence, seems to exclude these other factors.

As the testing sites cover a wide range of Australian low-altitude climatic conditions, it should be possible by interpolation to predict the loss of plasticizer at a given site if the average daily maximum temperature is known. As shown in Table I, this has been undertaken for Sydney, New South Wales, and an estimate has also been made based on the average daily mean temperature.[7]

The results quoted apply to the control PVC formulation without special additives. Compounds with improved resistance to weathering show less surface damage, which is reflected in a reduced loss of plasticizer. The
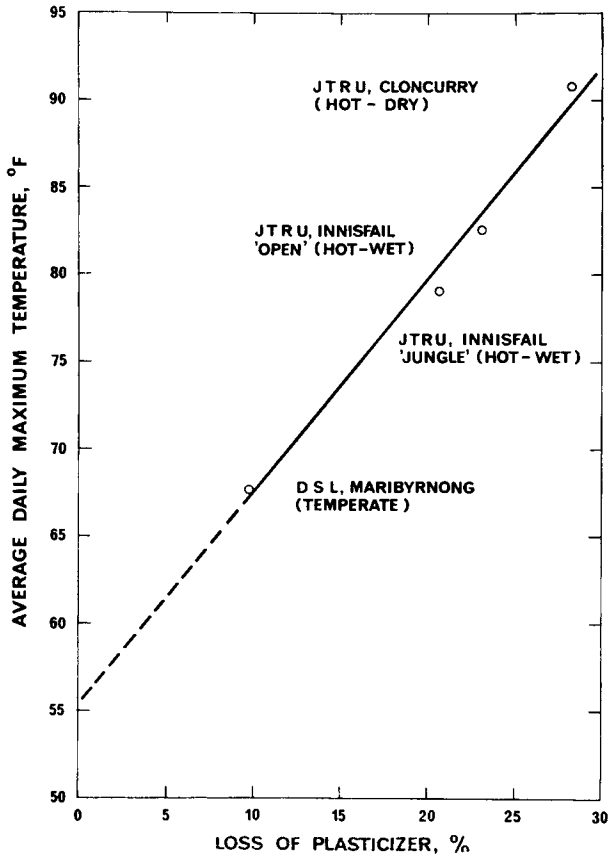
Fig. 1. Relation between average daily maximum temperature and loss of plasticizer for plasticized PVC compounds exposed for 4.5 years at four sites in Australia.

quality of the PVC compounds is thus of primary importance in the loss of plasticizer as a result of outdoor weathering.

From Figure 1, it would appear that PVC compositions containing di-octyl phthalate as the primary plasticizer, if stored below about 55°F, should show an insignificant rate of loss of plasticizer.

The results discussed apply to dioctyl phthalate which is one of the most commonly used plasticizers in Australia. By comparing the volatilities of other plasticizers with that of dioctyl phthalate, it should be possible to anticipate the long-term performance of these plasticizers over a wide range of climatic conditions.

Polymer Degradation During Exposure

Actinic degradation of PVC during exposure would be expected to cause changes in the molecular weight of the polymer. These changes should be able to be detected by viscosity measurements, and preliminary experi-

TABLE II
Plasticized PVC Exposed for 4.5 years[a]

Additive[b]	Cloncurry (hot-dry)	Innisfail (hot-wet)		Maribyrnong (temperate)	Average viscosity	Overall rating
		"open"	"jungle"			
S₁ + TBT fluoride	70.5	100.9	127.5	—	99.6	1
S₂ + TBT fluoride	68.9	97.1	116.0	—	94.0	2
S₁ + Ph₃SnF	70.7	105.4	98.0	89.2	90.8	3
S₁ + Poly(TBT methacrylate)	67.0	86.4	111.3	87.2	87.4	4
Bronze-green pigment	74.6	92.6	96.8	82.5	86.6	5
S₂ + Poly(TBT methacrylate)	75.7	78.7	97.4	94.3	86.5	6
S₂	68.9	97.1	91.0	—	85.6	7
Ph₃SnF	66.9	96.0	94.7	82.7	85.1	8
S₂ + Ph₃SnF	67.7	92.0	92.7	82.4	83.7	9
Poly(TBT acrylate)	65.9	92.1	95.3	80.5	83.4	10
TBT fumarate	63.2	88.4	96.3	79.9	81.9	11
Bis(TBT) terephthalate	46.1	90.9	102.8	80.1	79.9	12
TBT fluoride	61.5	92.4	80.7	—	78.1	13
Bis(TBT) oxide	62.9	77.9	94.6	74.5	77.5	14
Bis(TBT) maleate	58.2	87.0	86.3	75.8	76.8	15
Bis(TBT) sebacate	47.2	83.6	82.4	87.4	75.1	16
S₁	60.0	78.4	86.7	—	75.0	17
Poly(TBT methacrylate)	40.5	73.2	94.5	77.1	71.3	18
Control, no additive	57.8	67.3	71.7	—	65.6	19

[a] Control compound P15, containing 0.5% w/w of each additive as listed.
[b] S_2, 2-hydroxy-4-methoxybenzophenone; TBT, tri-n-butyltin; S_3, 2-(2'-hydroxy-5-methylphenyl)benzotriazole; Ph₃SnF, triphenyltin fluoride; bronze-green pigment was added at a concentration of 0.8% w/w (see experimental section for composition); TBT fumarate, tri-n-butyltin fumarate half ester, Advacide N628 (Advance Solvents and Chemical Company).

ments on unexposed PVC compounds showed that the inherent viscosity as determined was independent of the additive present. Viscosity data for specimens returned after long-term exposure at four separate sites are given in Table II.

Changes in the molecular weight of the polymer due to chain scission or to crosslinking as a result of actinic degradation are thus reflected in the inherent viscosity measurements. The specimens with the best resistance to weathering, as assessed by visual observation, had the highest viscosity. The viscosity values listed for each site are generally lowest at Cloncurry (hot-dry climate), and follow in increasing value at Maribyrnong (temperate), Innisfail (hot-wet) "open" and Innisfail "jungle." This general trend may reflect the climatic conditions at each site.

An average viscosity value for each compound over all the sites was then derived, and this was used to represent the overall performance of each additive. In Table II, the additives are arranged in descending order according to the average viscosity, and an overall rating is allocated to each. Although the lowest number in the overall rating scale indicates least degradation, care should be taken in interpreting results, as some variations in performance at different sites have been found.

Visual examination indicated that the surface color of the exposed specimens could vary from the original white to a dark brown, depending on the additive present. The surface discoloration of the compounds, particularly those exposed at Cloncurry, agreed well with the overall rating, as in all cases the lowest rating was associated with the least degree of surface discoloration. However, because of wide variations in surface texture and color at each site, inherent viscosity is seen as a more reliable parameter than surface color in assessing the relative efficiency of additives in reducing actinic degradation.

Of the best six compositions (Table II), five contained both an organotin compound and an ultraviolet absorber and performed better than compositions with one of these additives alone. This indicates that a powerful protective effect operates when these two classes of compound are present together. The use of the green pigment in the compound gave greater protection than either of the ultraviolet absorbers alone.

As shown in Table II, both tri-n-butyltin fluoride and poly(tri-n-butyltin methacrylate) in combination with either ultraviolet absorber were more effective in reducing actinic degradation than the ultraviolet absorbers alone. When used in combination with an organotin compound, the absorber S_1 (2-hydroxy-4-methoxybenzophenone) performed better than S_2 (2-(2'-hydroxy-5-methylphenyl)benzotriazole). However, when the ultraviolet absorbers were used alone with the standard PVC compound, the order of performance was reversed.

When the compositions containing only a single additive were considered, the order of rating of some of the additives was: green pigment (rating 5), ultraviolet absorber S_2 (rating 7), triphenyltin fluoride (rating 8), and ultraviolet absorber S_1 (rating 17). Thus, triphenyltin fluoride is exerting a

powerful protective effect and is only marginally worse than the better of the two ultraviolet absorbers.   Triphenyltin fluoride also exhibits a protective effect with the ultraviolet absorbers.

Changes in Physical Properties During Exposure

With plasticized PVC, changes in the plasticizer content can have a marked effect on the mechanical properties.   Because of the high loss of plasticizer caused by evaporation, the mechanical properties of the exposed compounds are affected by this loss as well as by degradation of the polymer.   In order to investigate these effects, compounds were prepared having a reduced plasticizer content, as shown in Table III.

TABLE III
Modified Formulations with Lower Plasticizer Content

	DSL compound no., parts by wt				
Component[a]	P108	P109	P110	P111	P112
PVC	100	100	100	100	100
Dioctyl phthalate	53.6	54.1	55.8	58.0	57.4
Octyl-9,10-epoxy stearate	8	8	8	8	8
Calcium carbonate	10	10	10	10	10
Tribasic lead sulfate	2.5	2.5	2.5	2.5	2.5
Dibasic lead phosphite	2	2	2	2	2
Calcium stearate	0.5	0.5	0.5	0.5	0.5
Bis (TBT) oxide		0.95			
TBT fluoride			0.95	0.95	0.95
S_1				0.95	
S_2					0.95
Plasticizer content, % w/w	34.8	34.8	35.5	36.1	35.9

[a] TBT, tri-n-butyltin; S_1, 2-hydroxy-4-methoxybenzophenone; S_2, 2-(2'-hydroxy-5-methylphenyl)benzotriazole.

Table IV compares the results of mechanical tests on the original specimens, the exposed specimens from Cloncurry and modified nonexposed specimens containing a reduced amount of plasticizer.

As shown in Table IV, a reduction in the amount of plasticizer in the compound causes changes in physical properties of the unexposed compound.   This indicates that mechanical measurements alone on exposed specimens should not be used as the sole evidence that the PVC itself has been degraded.   In particular, the tensile and tear strengths of the specimens seem to be most affected by the reduction in plasticizer content.

The elongation at break, however, which might be expected to be reduced by crosslinking in the polymer, is greatly reduced in exposed specimens as compared to both the unexposed originals and the modified specimens.   Compounds containing both organotin and ultraviolet absorber additives are less affected, suggesting that the protective effect as shown by viscosity rating is also being exhibited.   This is apparent from the me-

TABLE IV
Mechanical Measurements

Additive[a]	Condition[b]	Plasticizer present, %	Tensile strength[3]		Elongation at break,[4] %	Tear strength[4]		Hardness[5] IRHD
			psi	kN/m²	%	lbf/in.	kN/m	
Control	original	39.5	2120	14 600	348	276	48.3	79
Control	exposed	28.2	—	—	—	430	75.3	90
Control	modified	34.8	2260	15 600	304	289	50.6	82
Bis(TBT) oxide	original	39.3	2040	14 050	331	269	47.1	77
Bis(TBT) oxide	exposed	28.3	2000	13 800	60	430	75.3	96
Bis(TBT) oxide	modified	34.8	1980	13 650	326	330	57.7	79
TBT fluoride	original	39.3	2180	15 000	367	278	48.6	77
TBT fluoride	exposed	29.2	1950	13 450	80	300	52.5	95
TBT fluoride	modified	35.5	2150	14 800	318	306	53.5	77
S_1 + TBT fluoride	original	39.1	2250	15 500	336	287	50.2	76
S_1 + TBT fluoride	exposed	30.2	1970	13 600	90	390	68.2	85
S_1 + TBT fluoride	modified	36.1	1920	13 250	292	256	44.8	73
S_2 + TBT fluoride	original	39.1	2210	15 250	350	293	51.3	76
S_2 + TBT fluoride	exposed	29.9	1870	12 900	120	360	63.1	86
S_2 + TBT fluoride	modified	35.9	1910	13 150	296	250	43.7	72

a Control compound P15 containing 0.5% w/w of each additive as listed.
b Original, measured before exposure; exposed, measured after 4.5 years of exposure at Cloncurry; modified, measured without exposure on compounds containing reduced amount of plasticizer as listed in Table III.

chanical measurements. The elongation at break can thus be recommended as a meaningful mechanical test for evaluating the resistance of plasticized PVC to weathering.

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