

The Stabilizing Effects Of Dibutyltin Distearate On Some Properties Of Poly(Glycerol-Phthalate) Based Alkyd Coating Exposed To Outdoor Weather.

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ABSTRACT

The effects of weathering on poly(glycerol-phthalate) based alkyd coatings of the unstabilised and stabilised samples using varying amounts of dibutyltin distearate have been studied. The weathering and stabilization processes were monitored using infrared spectroscopy, gel formation, colour development, tensile strength as well as determination of time of embrittlement. The results showed that, relative to the control, there were, reduction in hydroxyl moiety formation, lack of discoloration, increased gel content, enhanced tensile strength and elongated life span of the stabilised alkyd coating, This indicated effective reduction in degradation reactions in the presence of the test tin ester. The 10×10^{-4} mole% dibutyltin distearate was the most effective concentration that stabilized the alkyd coatings.

INTRODUCTION

Alkyd resins constitute one of the oldest and yet one of the most versatile resins employed in the paints industry¹. They are polycondensates of polyols and dicarboxylic acids modified with monocarboxylic acid which is reacted with the extra (unpolymerised) hydroxyl groups of the polyols. The major drawback of alkyd coatings is poor outdoor durability. This has restricted its use mainly to indoor coatings if used alone. The major degradation reactions associated with alkyds during exposure to outdoor environment have been identified² as photodegradation due to the attack of the UVB component of the solar radiation and hydrolytic degradation due to acid rain. The level of such degradative reactions would be expected to be greater in tropical weather due to harsh sunshine, heavy rainfalls, and extreme harmattan as well as microbial components of the atmosphere.

In our previous articles^{3,4} an alkyd, poly(pentaerythritol phthalate), $[\text{OCOC}_6\text{H}_4\text{COOCH}_2\text{C}(\text{CH}_2\text{OCOR})_2\text{CH}_2\text{O}]_n$, called AFTALAT VAT 3324 in the resin industry, modified with tall oil containing about 10-15% w/w conjugated acid) was proved to be stabilized by some dibutyltin dicarboxylates under outdoor conditions. The present report is on a different alkyd, poly(glycerol phthalate) $[\text{OCOC}_6\text{H}_4\text{COOCH}_2\text{CH}(\text{OCOR})\text{CH}_2\text{O}]_n$ called Nycil 5960 STX, a styrene vinylated alkyd resin based on soyabean and dehydrated castor oil (DCO) containing 40-42% conjugated acid under the similar exposure. No two alkyds have the same properties in the coating industry⁵. Therefore individual study of the degradation-stabilization characteristics of alkyds, using any promising stabilizer under similar or different exposure conditions, is of paramount importance.

Although diorganotin compounds such as dibutyltin maleate and dioctyltin thioglycollate have been used extensively as stabilizers in polymers particularly PVC, their use as stabilizers for an alkyd exposed to a tropical weather has just been recently reported^{3,4}. The present work is to show the effectiveness of the compounds as a stabilizer for another alkyd system. A comparison will also be made between some of the properties of the two alkyd alkyds thereby justifying the need for the present work.

EXPERIMENTAL

Materials

AR 5960 STX resin, a poly(glycerol-phthalate)(PGP) based alkyd, was obtained from Nycil Ltd. Lagos. Gasoline used as the thinner was obtained from the petrol station, but dried over anhydrous calcium chloride for 48h and filtered before use.

Substrates

Glass sheet substrates were cut in dimensions of 10cm x 5cm x 0.2cm cleansed by washing with soap solution and rinsed with distilled water before leaving in a desiccators to dry.

Paper card film frames

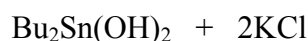
Cards of paper 5cm x 3cm dimension were cut out of cardboard sheets. With a clean razor blade round holes of 2cm diameter were cut on the paper cards for mounting films of test samples.

The infrared (ir) spectrophotometer used was an ATI-MATTSON USA GENESIS FTIR.

Synthesis and characterization of dibutyltin distearate

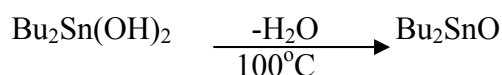
30.30g (0.1mole) of dibutyltin dichloride (Bu_2SnCl_2) was dissolved in 200cm^3 of diethylether in a 500cm^3 separatory funnel. 11.20g (0.2mole) of potassium hydroxide pellets was dissolved in 50cm^3

distilled water and the solution added to the ethereal solution of Bu_2SnCl_2 at room temperature. At about 30 minutes intervals the contents of the funnel were shaken for a period of 3h and thereafter left to stand for another 3hr. The white precipitate formed was filtered and purified as follows: unreacted Bu_2SnCl_2 was washed with ether until the filtrate did not produce any precipitate with KOH solution. The reaction is

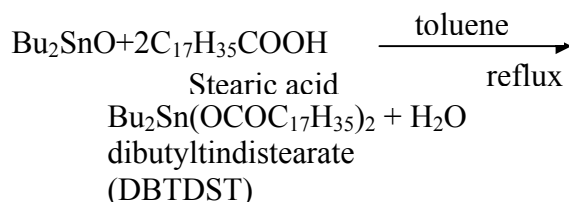


Any unreacted KOH was washed with distilled water until the filtrate did not show white precipitate after repeated tests with AgNO_3 solution.

The white precipitate ($\text{Bu}_2\text{Sn(OH)}_2$) was dehydrated by drying at 100°C to give dibutyltin oxide (Bu_2SnO).



24.8g (0.1mole) dibutyltin oxide was reacted with 56.8g (0.2mole) stearic acid ($\text{C}_{17}\text{H}_{35}\text{COOH}$) by refluxing in toluene for three hours using Dean-Stark apparatus to remove the azeotropic mixture of toluene and water. This is to enable the reaction favour formation of the ester.



The dibutyltin distearate, referred to herein as DBTDST, was characterized by tin analysis and infrared spectroscopy.

Tin analysis

Tin analysis was carried out using the method reported by Farnsworth and Pekola⁶. 0.2g of DBTDST was weighed separately into three clean and previously weighed sintered crucibles. 1.50cm³ of concentrated H₂SO₄ (98%) was added and the mixture heated from the top using bunsen flame until all the SO₂ fumes were given off. A dark yellow residue was obtained which was further heated with the flame applied under the crucible placed on a clay triangle on top of a tripod stand. The crucible was burnt thoroughly to remove any carbon deposit. After cooling in a desiccator for 15hr the crucible/SnO₂ was weighed to obtain the mass of SnO₂ by difference. The average of three weights of SnO₂ was obtained. The tin content of the DBTDST was calculated from the expression:

$$\%Sn = \frac{\text{atomic mass of Sn} \times \text{mass of SnO}_2}{\text{molar mass of SnO}_2 \times \text{mass of DBTDST}(0.2g)} \times 100$$

The experimental %Sn was compared with the theoretical value of Sn in DBTDST. Further characterization of the tin ester was carried out using infrared spectroscopy as earlier reported⁷.

Incorporation of tin ester into resin and preparation of coatings

Into a 2000cm³ quickfit conical flask place 100g of PGP resin and 0.399g (5x10⁻⁴moles) of DBTDST. 50cm³ of thinner (petrol) was then added to the mixture which was thermostated at 35°C in a water bath and stirred mechanically for 100 minutes. 10cm³ of the homogenous liquid was poured onto a glass sheet(10cm X5cm) and allowed to dry at room temperature. This procedure was repeated twice using 0.798g (10x10⁻⁴ mole) and 1.596g (20x10⁻⁴ mole) of DBTDST respectively. Thus, for quantitative comparison, the number of mole contained in 100g of resin as employed in previous works^{3,4,8,9,10} was used in the present work. These three

samples referred to herein as the stabilized samples, therefore, contained 5, 10 and 20x10⁻⁴ mole % DBTDST respectively. Using another clean quickfit conical flask, the above procedure was repeated without the tin ester. This served as the control sample.

Outdoor ageing of Coatings

Glass sheet (10cm x 5cm x 0.2cm) coated with the control (resin alone) and stabilized samples were mounted on a specially prepared plywood shelve. The plywood shelve was then placed on a roof top so that the glass plates rested at an angle of 45⁰ to the horizontal.

Determination of hydroxyl (-OH) index

Films of about 0.02cm thickness were removed from the coatings which had set on the glass plates previously exposed on the roof using clean razor blade and placed over the rounded holes(2cm diameter), carved out in paper cards previously. This is to allow ir penetration during the running of the spectra. Thus, spectra of the control and stabilized films (coatings) were obtained at 200 hourly intervals of exposure to outdoor conditions. The -OH index was obtained using expression similar to one reported earlier.^{3,4,9,10}

$$-OH \text{ index} = \frac{\text{Absorbance at } 3450\text{cm}^{-1}}{\text{Absorbance at } 1605\text{cm}^{-1}}$$

The -OH absorbance is at about 3450cm⁻¹ relative to that of the C=C of benzene at 1605cm⁻¹. The latter absorbance was constant during the period of exposure to outdoor environment and was used as the reference absorbance.

Determination of gel content

0.10g each of the dry control and stabilized samples was separately weighed into a 20cm³ volumetric flask. Petrol was added to mark, stoppered and

left for 72 hours in the dark at room temperature with periodic shaking. Thereafter the content was filtered and the residue (gel) was thoroughly washed with petrol and dried to constant weight in the oven at 80°C.

The gel content (%) was determined from the expression:

$$\text{Gel content (\%)} = \frac{\text{Mass of insoluble fraction} \times 100}{\text{Initial mass of coating (0.10g)}}$$

The above procedure was repeated at 200h, 400h and 600h exposure times.

Determination of embrittlement time (ET) of coatings

The time it takes an exposed film to crack is the embrittlement time, usually determined in hours. The method earlier reported^{3,4,8,9,10} was used. It involved bending the film forward and backward through 180° at the 200 hourly intervals of exposures until it cracked.

Determination of tensile strength (TS) of coatings

At 200 hourly intervals of exposure, coatings of 3cm x 1cm and 0.02 ± 0.001cm thickness were neatly removed with a clean razor blade and stretched using the INSTRON Tensile Testing machine Model 1026. The gauge length of 1.0cm was used. The stress-strain curves at 0h and at intervals of exposure to natural weather were plotted from which the tensile strengths (see Figure 1 under 'results and discussion') were obtained as:

$$\text{Tensile strength (Nm}^{-2}\text{)} = \frac{\text{Breaking Load (N)}}{\text{Cross-sectional area (m}^2\text{)}}$$

RESULTS AND DISCUSSION

Synthesis of dibutyltin distearate

Table 1 shows the melting point, result of tin analysis and important i.r. absorptions of DBTDST. The tin analysis gave credence to the successful synthesis of the tin ester as the calculated values compare well with the experimental values.

Table 1: Melting point, tin content and important infrared bands

Properties	M.pt. (°C)	% Sn Calc.	% Sn Found	$\nu_{\text{(Sn-Bu rock)}}$ cm^{-1}	$\nu_{\text{(C=O assym)}}$ cm^{-1}	$\nu_{\text{(Sn-O-C stretch)}}$ cm^{-1}
DBTDST (cm^{-1} , NaCl) of DBTDST	59-61	14.90	15.05	660(m)	1550(s)	985(w)

The ir results were in agreement with the reported bands of Sn-Bu (rock), C=O (assym) and Sn-O-C (stretch) absorption bands⁷. These confirm the synthesis of the tin ester.

Oxidation of PGP coatings

Table 2 shows that the level of formation of hydroxyl compounds is generally higher in the control sample than in the samples containing the

varying amounts of the DBTDST. The coatings containing 5 and 10×10^{-4} mole% DBTDST have lower -OH indices, in that order, throughout the period of exposure while the 20×10^{-4} mole % of the additive is generally ineffective in lowering the formation of the -OH compounds. The sample

containing 10×10^{-4} mole % DBTDST with an induction period of 400h, generally showed the least levels of formation of hydroxyl moiety suggesting that the test tin ester(at 10×10^{-4} mole %) can effectively retard oxidative reactions when incorporated into the PGP coating exposed to weather.

Table 2: Effect of outdoor exposure on the hydroxyl index of PGP alkyd coatings

Sample	Hydroxyl Index			
	Exposure time (h)			
	0	200	400	600
Control (no additive)	2.52	2.40	2.00	1.94
5×10^{-4} mole% DBTDST	1.90	1.80	1.80	1.80
10×10^{-4} mole% DBTDST	1.71	1.71	1.71	1.75
20×10^{-4} mole% DBTDST	2.00	2.30	2.00	2.10

Formation of -OH compounds during exposure to outdoor conditions has been attributed to oxidative reactions which are detrimental to the desired properties of polymer films⁸⁻¹⁰. The oxidation is initiated by the formation of free-radicals due to bond-breaking effect of the UV component of the sunlight on the coatings or films².

Gel formation

Table 3 gives the gel content of the coatings before exposure to weather. The coatings containing the tin esters have higher gel than the control at 0h and during outdoor exposure. The coating containing the 10×10^{-4} mole% DBTDST had the greater formation of gel from the onset of exposure.

Table 3: Gel content(%) of PGP coatings during outdoor exposure

Sample	Exposure time (h)			
	0	200	400	600
Control (no tin ester)	20	60	65	80
5×10^{-4} mole% DBTDST	60	60	70	85
10×10^{-4} mole% DBTDST	80	90	99	99
20×10^{-4} mole% DBTDST	30	70	80	80

The formation of gel is expected to reduce the level of diffusion/penetration of oxygen into the polymer matrix and so reduce the level of oxidative degradation. The higher gel contents in the coatings containing the test tin ester suggest that

the coatings may not be easily oxidized as the control would.

The most probable explanation for these results could be that the thermally sensitive Sn-O bond⁸ in the ester

homolyses yielding, first, the dibutyltin carboxylate radical which can scavenge a polymer radical. The process is repeated until both carboxylate groups in the DBTDST are replaced. Such process will not only reduce the amount of polymer radicals but cross link the polymer chains. The resulting Sn – C is most probably less vulnerable to thermal decomposition than the Sn – O bond in the tin ester, the Sn – C covalent bond being possibly stronger. The relative strength is based on the fact that the homolytic fission of Sn – C or Sn – O bond is decided by the resultant electronegativity of Sn and the moiety of carbon groups attached to it or oxygen and the group attached to it. Therefore, while the electronegativity difference between Sn and C or Sn and O may be such that encourages heterolytic fission, the pattern of fission will be the same where the C and O are bonded to groups which alter their electronegativities and make them comparable to that of Sn. Consequently, the relative values of thermal parameters are not available to us.

The results of oxidation and gel formation (Tables 2 & 3) showed that stabilization due to retardative oxidation and increasing gel formation occurred by incorporating 5-10 x 10⁻⁴ mole % DBTDST and increased oxidation at 20 x 10⁻⁴ mole % of the additive. This may be

attributed to excessive dibutyltin radicals obtained at the higher concentration which could abstract C-H protons from the polymer (alkyd) chain to produce more of Sn-H and oxidation of polymer chain rather than the formation of Sn-C in the stabilization reaction

Colour development

The visual observation of colour employed in previous work is used here¹⁰. Thus, the colour at 0h is the preexposure colour of all samples and the colours at intervals of 200h up to 600h of exposure to outdoor conditions were observed. Colour change from relatively transparent to yellow films has been attributed to development of conjugated unsaturation¹¹. Table 4, therefore, shows that the growth of conjugated unsaturation generally occurred faster in the control than in the coatings containing the test tin ester. It took the control less than 200h from the commencement of exposure to change from colourless to light yellow while the samples containing 5, 10 and 20 x 10⁻⁴ mole% DBTDST had similar colour change after about 400h, 600h and 200h respectively. Conjugated unsaturation has been implicated as the precursor to early deterioration of important properties of PVC¹¹ during service life. Thus, the

Table 4: Colour development in PGP coatings during outdoor exposure

	Exposure time (h)			
	0	200	400	600
Control (no tin ester)	colourless	light yellow	yellow	Deep yellow
Resin + 5 x 10 ⁻⁴ mole% DBTDST	colourless	colourless	colourless	light yellow
Resin + 10 x 10 ⁻⁴ mole% DBTDST	colourless	colourless	colourless	colourless
Resin + 20 x 10 ⁻⁴ mole% DBTDST	colourless	colourless	light yellow	light yellow

presence of the tin esters effectively delayed the formation of conjugated unsaturation thereby stabilizing the PGP alkyd coating against outdoor degradants.

Tensile strength (TS)

Figure 1 shows the variation in the tensile strength of the control sample and coatings containing 5, 10 and 20 x 10⁻⁴ mole% DBTDST. It can be seen that while the tensile strength of the control sample decreased sharply with increasing exposure time, the tensile strength of the coatings containing the test tin ester was generally constant. This can be seen from Figure 1 that after the embrittlement of the control sample at about 800h outdoor exposure, the coatings containing 10 x 10⁻⁴ mole% of the test tin ester still had tensile strength values of about 20 x 10⁶ Nm⁻². The presence of the tin ester, particularly at 10 x 10⁻⁴ mole%, could have enhanced the rigidity of the coating probably by increased gel formation as shown in an earlier section.

Mechano-chemical scission has been implicated for the initial degradation of polymers¹¹. In Figure 1 the initial TS values (at 0hr) showed that the processing had different effects on the unstabilized

and stabilized PGP coatings. The TS of the coating containing 10 x 10⁻⁴ mole% DBTDST was least deteriorated while that of the unstabilized was most adversely affected. Thereafter, the reduction levels in TS values during exposure were very minimal for samples stabilized with 10 x 10⁻⁴ mole% DBTDST. For instance its TS value is 22 X 10⁶Nm⁻² at 0h which reduced to 20 x 10⁶Nm⁻² at 800h i.e. 9.09% reduction.

The greatest reduction level in TS value(77.78%) occurred in the unstabilized samples within the same period (i.e. 9x10⁶Nm⁻² at 0h reduced to 2 x 10⁶Nm⁻² at 800h).

Embrittlement time (ET)

The embrittlement time is the life span index of any coating or film¹¹. It can be seen in Table 5 that the coatings containing DBTDST generally had longer ET than the control. The 10 x 10⁻⁴ mole% DBTDST was most effective in prolonging the life span of the PGP alkyd coating during outdoor exposure for about 400h (1200h-800h).

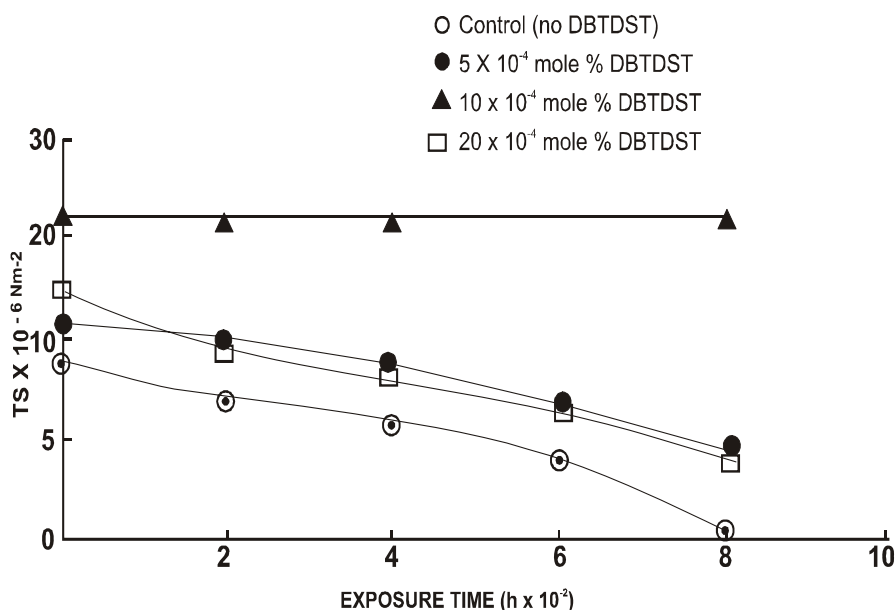


Fig. 1: Weatherability of PGP. Effect of DBTDST on the tensile strength of PGP during outdoor ageing.

Table 5: Embrittlement time (h) (to nearest tens) of PGP alkyd Coatings during outdoor exposure

Sample	Embrittlement time (h)
Control (no additive)	800
5 x 10 ⁻⁴ mole% DBTDST	800
10 x 10 ⁻⁴ mole% DBTDST	1200
20 x 10 ⁻⁴ mole% DBTDST	1000

The present results show that the degradation and stabilization of the alkyd used in the previous study are quite different from those of the alkyd employed in the present study (see Tables 6 and 7)

Table 6. Hydroxyl index in two Alkyd samples during outdoor Exposure

Exposure time(h)	Alkyd (I)		Alkyd (II)	
	Control	Hydroxyl Index 10 X 10 ⁻⁴ mole% DBTDST sample	Control	10 X 10 ⁻⁴ mole% DBTDST sample
0	1.60	1.60	2.52	1.71
200	1.20	1.30	2.40	1.71
400	1.70	1.40	2.00	1.71
600	-	-	1.94	2.10

Alkyd I = poly (pentaerythritol – phthalate) modified with tall oil
Alkyd II = poly (glycerol- phthalate) modified with styrene based on soyabean and dehydrated castor oil.

Table 7 Gel content in two alkyd samples during outdoor exposure.

Exposure time(h)	Alkyd I		Alkyd II (%)	
	Control	Gel content (%) 10 X 10 ⁻⁴ mole% DBTDST sample	Control	10 X 10 ⁻⁴ mole% DBTDST sample
0	86	85	20	80
200	72	86	60	90
400	62	90	65	99
600	-	89	80	99

Alkyd I – poly (pentaerythritol – phthalate) modified with tall oil
Alkyd II – poly (glycerol -phthalate) modified with styrene based on soyabean and dehydrated castor oil.

Moreover, the embrittlement times of the control samples were 500h and 800h for alkyds I and II respectively. The embrittlement times of the samples stabilized with 10×10^{-4} mole% DBTDST are 1600h and 1200h for alkyds I and II respectively. These differences are consistent with the view that no alkyds have the same degradation and/or stabilization characteristics². However two other technological parameters i.e. color development and tensile strength, were studied in the present work (in alkyd II) which were not considered in the previous article even though the alkyds were stabilized with DBTDST under similar outdoor environment.

CONCLUSION

The results presented in this article generally point to DBTDST as a possible stabilizer that can redeem PGP based alkyd coating from early deterioration during weathering. The stabilizing activity of the organotin ester can be summarized as follow :

1. The presence of dibutyltin distearate retards formation of oxidation products via a competing reaction between atmospheric oxygen and dibutyltin radicals for polymer chain radicals. Such reaction reduces the amount of macroalkyl radicals that yields oxidized polymer chains.
2. There was generally increased gel in the presence of dibutyltin distearate. This acted, most probably, as a surface covering for reducing further penetration of oxygen into the polymer matrix and hence reduced the level of oxidative degradation of the PGP based alkyd coating.

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accepted 19/10/005

received 20/7/005