

(which run along the a -axis) formed by type II protons linking type II sulphate ions [10]. The E_f value of 0.80 eV probably represents the energy required to delink the polymeric chain, to form either free protons or relatively free HSO_4^- units which could reorient itself, resulting in proton jumps. The formation of K^+ vacancies, however, is equally probable. Thus, in the Cu^{2+} -doped KHSO_4 crystal, the extrinsic conduction is likely to proceed via migration of proton interstitials as well as K^+ vacancies, and, the former seem to be present in appreciable concentration even in the undoped KHSO_4 crystals.

Dielectric loss measurements on these crystals are expected to throw more light on the nature of the charge-compensating defects.

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Pigment anti-oxidant interactions: a simple numerical analysis

In a previous publication [1] we presented experimental results of the stabilizing action of eight anti-oxidant combinations in pigmented low-density polyethylene after accelerated weathering in a Xenotest-150. Six commercial rutile pigments were used in the sample formulations. In this letter we present a simple algebraic method of assessing the polymer degradation data to estimate the extent of pigment/anti-oxidant interaction. The pigment/anti-oxidant interaction values obtained are discussed in relation to the anti-oxidant efficiency in pigmented polyethylene. Experimental details are given in the previous paper [1].

The carbonyl indices of all 63 samples after 500h accelerated weathering are summarized in Table I. Assuming there is no interaction between anti-oxidants and pigments the effect of both components in a single system will be the sum of the pigment/polymer interaction and the polymer/anti-oxidant interaction.

The pigment interaction with the polymer PIP may be defined as:

$$\text{PIP} = \text{C.I.}(\text{usup}) - \text{C.I.}(\text{usp}) \quad (1)$$

where $\text{C.I.}(\text{usup}) =$ carbonyl index after t h irradiation of an unstabilized, unpigmented polymer film, an $\text{C.I.}(\text{usp}) =$ carbonyl index after t h irradiation of an unstabilized, pigmented polymer film. When written this way, a positive value of PIP indicates a stabilizing action and conversely, a negative value indicates a sensitizing action by the pigment.

In a similar way, the anti-oxidant/polymer interaction (PIAO) can be written as:

$$\text{PIAO} = \text{C.I.}(\text{usup}) - \text{C.I.}(\text{sup}) \quad (2)$$

where $\text{C.I.}(\text{sup}) =$ carbonyl index after t h irradiation of a stabilized, unpigmented system. A positive value for PIAO indicates a stabilizing action and, conversely, a negative value indicates a sensitizing effect by the anti-oxidant.

Hence by combining Equations 1 and 2 a value for the carbonyl index after t h irradiation of a stabilized, pigmented system $\text{C.I.}(\text{sp})^{\text{calc}}$ can be predicted:

$$\text{C.I.}(\text{sp})^{\text{calc}} = 2\text{C.I.}(\text{usup}) - \text{C.I.}(\text{sup}) - \text{C.I.}(\text{usp}) \quad (3)$$

The ratio of this value with the actual value of $\text{C.I.}(\text{sp})$ will give a numerical value (AOPI) of the

anti-oxidant/pigment interaction,

$$\text{i.e. AOPI} = \frac{2\text{C.I.}(usup) - \text{C.I.}(usp) - \text{C.I.}(sup)}{\text{C.I.}(sp)} \quad (4)$$

A value for AOPI of unity indicates zero anti-oxidant/pigment interaction, a value greater than 1 indicates favourable overall interaction and a value between unity and zero indicates an overall sensitizing interaction of pigment/anti-oxidant combinations in the polymer. A negative value indicates that the pigment sensitizing action is greater than the anti-oxidant stabilizing action. (This is assuming, of course, that the anti-oxidant is, in fact, a stabilizer). The values from Table I have been substituted into Equation 4 and summarized in Table II.

It must be stressed that the values of AOPI given in Table II indicate the extent of interaction between the anti-oxidant and the pigment, and not necessarily the degree of stabilization of the

polymer in which they are incorporated. The closer the modulus of the value to unity, the less the interaction of the anti-oxidant with the pigment.

The negative AOPI values for all anti-oxidant combinations in the presence of pigment I indicate that the sensitizing action of the pigment is only slightly reduced. Further, with this pigment the primary/secondary anti-oxidant combinations Topanol CA/DLTDP and Irganox 1010/Weston 618 exhibit the least interaction and, from Table I, the greatest stabilizing effect. The two secondary anti-oxidants, Weston 618 and DLTDP and the primary/secondary combination Topanol CA/Weston 618, interact most strongly with this pigment and exhibits a correspondingly weak stabilizing effect.

One can now make the generalization that the greater the anti-oxidant combination/uncoated pigment interaction the lower the efficiency of the anti-oxidant combination in stabilizing the polymer.

TABLE I Carbonyl index (10^{-3} m^{-1}) after 500 h irradiation in a Xenotest-150

Anti-oxidant (0.1% phr)	Pigment (1% phr)*						
	1	2	3	4	5	6	None
None	3.12	1.88	1.10	0.98	0.88	0.70	1.65
Topanol CA	2.00	0.80	0.37	0.80	0.50	0.55	1.20
Irganox 1010	1.38	0.65	0.14	0.25	0.18	0.20	0.95
DLTDP	2.62	1.40	0.75	0.88	1.14	0.55	0.95
Weston 618	2.12	1.60	0.88	0.80	0.75	0.70	0.95
Topanol CA + DLTDP	0.95	0.80	0.37	0.51	0.50	0.25	0.93
Topanol CA + Weston 618	2.12	1.30	0.35	0.70	0.52	0.40	0.95
Irganox 1010 + DLTDP	1.62	0.95	0.20	0.30	0.25	0.22	0.90
Irganox 1010 + Weston 618	1.25	1.00	0.20	0.32	0.25	0.27	1.00

*Parts per hundred resin.

TABLE II AOPI values calculated from Table I ($t = 500 \text{ h}$)

Anti-oxidant (0.1% phr)	Pigment (1% phr)					
	1	2	3	4	5	6
Topanol CA	-0.51	0.28	2.70	1.40	2.44	2.55
Irganox 1010	-0.56	0.72	8.93	5.48	8.17	8.25
DLTDP	-0.29	0.34	1.67	1.56	1.29	3.00
Weston 618	-0.36	0.29	1.42	1.53	1.96	2.36
Topanol CA + DLTDP	-0.80	0.61	3.43	2.73	2.98	6.68
Topanol CA + Weston 618	-0.36	0.36	3.57	1.96	2.83	4.13
Irganox 1010 + DLTDP	-0.45	0.55	6.50	4.74	6.08	7.73
Irganox 1010 + Weston 618	-0.66	0.42	6.00	4.13	5.68	5.93

In the case of the four coated pigments, the general rule is the reverse of that for uncoated pigments i.e. the greater the anti-oxidant/coated pigment interaction the greater the stabilizing efficiency of the anti-oxidant. Further, the presence of secondary anti-oxidants have a significant influence on the interaction of primary anti-oxidants with coated and uncoated pigments. For example DLTDP and Weston 618 both reduce the interaction of Irganox 1010 with all the coated pigments and increase the interaction with uncoated pigments.

Finally, the following four general conclusions may be drawn from the results.

(1) The extent and type of interaction between pigments and anti-oxidants in polyethylene dictates the overall stabilizing efficiency of a particular anti-oxidant in a pigmented L.D.P.E. system.

(2) The greater the anti-oxidant combination/uncoated pigment interaction the smaller the stabilizing effect in the polymer.

(3) The greater the anti-oxidant combination/coated pigment interaction the greater the stabilizing effect in the polymer.

(4) Secondary anti-oxidants can increase or decrease the interaction of pigments with primary anti-oxidants. This is, in turn, dependent on the pigment and the anti-oxidant combinations but is consistent with (2) and (3) above.

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