ment), hence their –COOH assessment is subject to several uncertainties.

The results of our work give direct confirmation to Owens' hypothesis[2] that enolic –OH is involved in the enhanced autoadhesive bonding of discharge treated polyethylene. The fact that it is also crucial to the mechanism of ink adhesion to such a surface seems to indicate the more general importance of this functional group in adhesion.

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Craze-proof bromostyrene–crosslinked polyester

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A novel phenomenon regarding craze resistance of bromostyrene*–crosslinked polyesters has been discovered while performing a group of studies on flame retardancy and other physical properties of these resins[1–4]. In these studies an alkyd resin composed of equal proportions of propylene glycol and of phthalic and furaric acids was crosslinked by a series of styrene/bromostyrene monomer mixtures. The total amount of crosslinking monomer amounted to 0.0048 moles per 1 g alkyd, resulting in a ratio of 2 moles of styrene/bromostyrene to 1 mole of alkyd double bonds. Six resin compositions were tested, in which the mole fraction of the bromostyrene of the total monomer amount was 0, 0.2, 0.4, 0.6, 0.8 and 1.0.

The assessment of the weathering stability of the resins included exposures of thin polyester plates to boiling water for different treatment periods. It was noted that whereas crazes were formed readily on the surface of the pure styrene-crosslinked polyesters, the tendency of craze formation decreased gradually as the bromostyrene proportion increased, and disappeared completely in the pure bromostyrene-crosslinked polyester. *Figure 1* presents a series of such plates after 12 h of water–boil treatment, and the gradual disappearance of crazing is clear. When the water–boil treatment laster for a longer period of time the crazes – where formed initially – resulted in disintegration of the polyester plates. In bromine containing plates, where craze formation was inhibited, round swells developed gra-

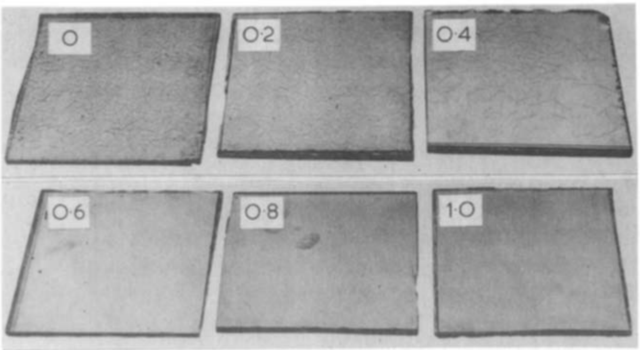

Figure 1 Polyester plates exposed to boiling water for 12 h. The numbers denote mole fraction of bromostyrene of total monomer

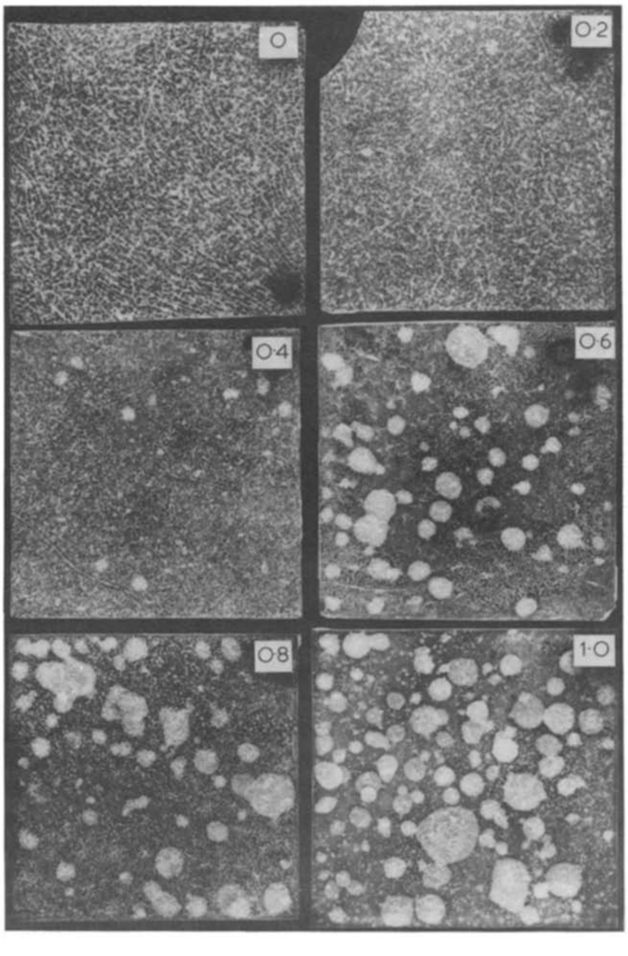

Figure 2 Polyester plates exposed to boiling water for 66 h photographed against a black background. The numbers denote mole fraction of bromostyrene of total monomer

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* Supplied by Makhteshim Chemical Works Ltd., Israel

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dually. A series of such plates is presented in *Figure 2*.

It is important to note that the residual ultimate strength of the polyesters after the water–boil treatment increased with the bromine content – consistent with the inhibition of craze formation[2].

We do not have, as yet, a sufficient explanation of the craze-preventive action by the bromine. It is impossible that the bulkiness of the bromine atom results in increasing the free volume of the polyester. Thus, penetration of more water molecules is allowed before the swelling stresses which gradually build up match the yield stress of the polymer and cause crazing.

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Glass transition temperatures and molecular weight*

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In a recent paper, it was shown that the dependence of the glass transition temperature, T_g, on the molecular weight, M, was given by an equation of the form (1)

$$T_g = T_{g,\infty} - \frac{A}{M+B} \qquad (1)$$

where $T_{g,\infty}$ is the limiting glass transition temperature of the polymer of infinite molecular weight and A and B are parameters whose values depend on the chemical structure of the polymer. It was demonstrated that this expression was applicable to several liquids over wide ranges of molecular weight, including the low molecular weight region, using a single value for each of the parameters A and B.

Since the publication of ref 1, it was found that earlier work by both Fox and Loshaek[2] and by Kanig[3] also led to an equation of the same form as equation (1). We should now like to discuss these two approaches in turn and point out that although the equations are of the same form, the assumptions used in the derivations are incorrect since they lead to physically impossible situations.

The equation of Fox and Loshaek can be expressed as:

$$T_g = T_{g,\infty} \frac{\alpha_\infty - C - \dfrac{(m+m_e)\Delta\nu_0}{T_{g,\infty}M}}{\alpha_\infty - C + \dfrac{(m+m_e)\Delta\alpha}{M}} \qquad (2)$$

where α_∞ is the slope of the volume-temperature response for a polymer with infinite molecular weight, C is a constant for a given polymer, m and m_e are the molecular weights of the repeating unit and the two chain ends, respectively, $\Delta\nu_0$ is defined as $\nu_0(1) - \nu_0(\infty)$ where $\nu_0(1)$ and $\nu_0(\infty)$ are the specific volumes of the liquid having one monomer unit and an infinite number of monomer units at $T = 0$, respectively and $\Delta\alpha = \alpha_l = \alpha_\infty$ where α_l is the slope of the V, T response for the liquid containing one monomer unit.

Simple manipulation of equation (2) leads to

$$T_g = T_{g,\infty} - \frac{A}{M+B}$$

which is identical to equation (1). Here, A has the value

$$A = \left(\frac{m+m_e}{\alpha_\infty - C}\right)\left(\Delta\nu_0 + \Delta\alpha T_{g,\infty}\right) \qquad (3)$$

and B can be expressed as

$$B = \frac{m+m_e}{\alpha_\infty - C}\,\Delta\alpha \qquad (4)$$

Using these results the ratio A/B becomes

$$\frac{A}{B} = \frac{\Delta\nu_0}{\Delta\alpha} + T_{g,\infty} \qquad (5)$$

Thus, by examining the ratio rather than the individual values themselves it is possible to eliminate the parameter B whose value is generally unknown. This last expression can be rearranged to yield:

$$\frac{\Delta\nu_0}{\Delta\alpha} = \frac{A}{B} - T_{g,\infty} \qquad (6)$$

The fit of equation (1) to the experimental T_g,M data for several series of liquids permit one to obtain values of A, B and $T_{g,\infty}$ and thus from these values the ratio $\Delta\nu_0/\Delta\alpha$ can be calculated. The requisite data are given in *Table 1* which is obtained from ref 1. From the values of $A/B - T_{g,\infty}$ listed

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