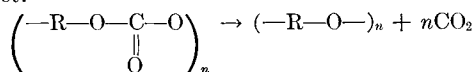


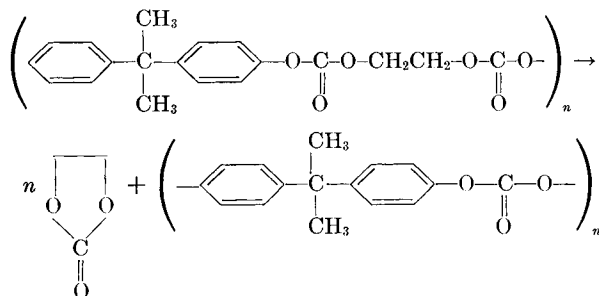
NOTES

Elimination of Ethylene Carbonate from Poly[ethylene co 2,2-bis(4-phenylene)propane Carbonate]

Pyrolysis of polycarbonates can, in some instances, yield polyethers. Thus J. W. Hill pyrolyzed poly(decamethylene carbonate) and obtained poly(decamethylene oxide) as one product:¹



Attempts to apply the same reaction to the polycarbonate derived from ethylene bischloroformate and diphenylolpropane did not give a polyether, but instead ethylene carbonate was rapidly and quantitatively eliminated leaving diphenylolpropane polycarbonate. The overall reaction was thus:



The residual diphenylolpropane polycarbonate was light yellow, clear, and tough, apparently of high molecular weight. Films were prepared either by dry casting from chloroform or by the usual melt pressing techniques. That the residual polymer was diphenylolpropane polycarbonate was conclusively shown by identity of its infrared spectrum to that of General Electric's Lexan* polycarbonate resin and to the same polymer prepared by interfacial polymerization² from diphenylolpropane and diphenylolpropane bischloroformate.

EXPERIMENTAL: Pyrolysis of Poly[ethylene co 2,2-bis(4-phenylene)propane Carbonate]

Poly[ethylene co 2,2-bis(4-phenylene)propane carbonate] was prepared from diphenylolpropane and ethylene bischloroformate by interfacial polymerization using methyl ethyl ketone as the organic phase and aqueous sodium hydroxide as acid acceptor. The polymer thus obtained was soluble in dimethylformamide and melted at 170°C. on a Dennis temperature gradient bar. This polycarbonate (η_{inh} 0.9 at 0.5% concentration and 30°C. in tetrachloroethane/phenol, 40/60 by weight) was heated at 280°C. and 1 mm. Hg pressure for 1 hr. Vigorous effervescence occurred and a colorless liquid distilled, which was identified as ethylene carbonate. The polymeric residue was cooled under nitrogen, dissolved in chloroform, and reprecipitated into methanol. The precipitate was then filtered and dried at 60°C. *in*

vacuo. Clear tough films were obtained by pressing the polymer at 240°C. in a Carver press or by dry casting from chloroform. The polymer melted at 240°C. on a Dennis temperature gradient bar and had an inherent viscosity at 0.5% concentration in tetrachloroethane/phenol (40/60) of 0.45. The polymer was shown to be diphenylolpropane polycarbonate.

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Stabilization of Polyethylene by Antioxidants of Large Particle Size

Carbon blacks which are used to inhibit photo-oxidation of polyolefins also function as mild thermal antioxidants. It has been suggested¹ that carbon black functions as a radical trap in terminating thermal oxidation. Antioxidant effectiveness has also been attributed to the presence of reactive groups on the particle surface.² The latter hypothesis is substantiated by the fact that effectiveness in chain termination increases with the concentration of these functional groups. Various investigators³⁻⁵ have identified these groups as hydroxyl, carbonyl, carboxyl, and lactone.

The effect of temperature on the oxidation rate of polyethylene inhibited with carbon black is different from that observed with the uninhibited polymer or with polyethylene containing molecularly dispersed antioxidants.⁶ With carbon black as the antioxidant, protection of the solid polymer is far greater than the extrapolated value based on accelerated oxidation above the polymer melting range. This results in a nonlinear relationship between oxidation temperature ($1/T$) and degree of protection (expressed as the logarithm of the induction period) in the temperature range of 80-160°C. Increased protection in the solid polymer has been confirmed by the observation that addition of 1% carbon black prevented significant loss in the physical properties of polyethylene during outdoor exposure in Florida for more than 18 years.¹

Oxidation of semicrystalline polymers has been assumed to occur principally in the amorphous regions.⁶ Also, it has been shown by density and x-ray studies that the overall crystalline content of polyethylene is not reduced by addition of 3% carbon black. Thus, there is an apparent increase in carbon black concentration with respect to the amorphous (oxidation-susceptible) region which results in greater protection in the solid polymer. Molecularly dis-

* Trademark for General Electric's polycarbonate resin.

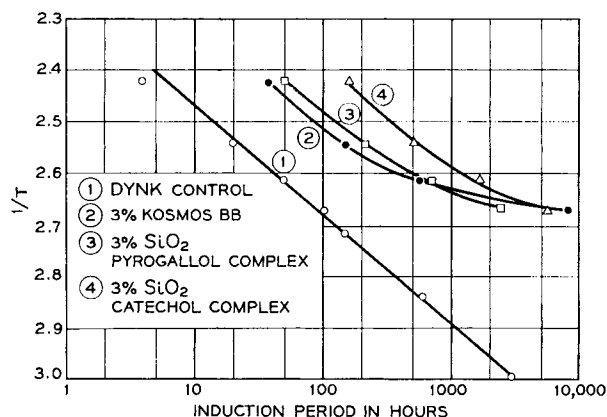
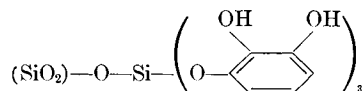


Figure 1.

persed antioxidants which may diffuse through the solid polymer show a linear relationship between $1/T$ and the induction period, but for antioxidants of large particle size, such as carbon black, this relationship diverges from linearity approximately at the polymer melting range.

Nonblack antioxidants in the particle range of carbon black have now been prepared by chemically bonding antioxidant groups to an inert particle surface. Silicon dioxide particles (10 g.) having an average mean diameter of 200 Å, approximately that of carbon black used to inhibit photo-oxidation, is reacted in carbon tetrachloride solution (210 cc.) with silicon tetrachloride (10 cc.). After refluxing for 2 hr., the unreacted halide is distilled off with about 10 cc. of the solvent. Pyrogallol (10 g.) is added and the reaction mixture refluxed for an additional 2 hr. The pale lavender complex which forms and may be represented schematically



is separated by filtration, washed twice with benzene, and dried in a vacuum desiccator. A similar complex has been prepared in which catechol was the phenolic component of the reaction. The organic surface coatings could not be extracted from the silica particles with organic solvents, and, on pyrolysis, the treated silica had a volatile loss several per cent higher than that of silicon dioxide comparably conditioned.

Approximately 3 g. of the complex was added to 100 g. of branched polyethylene by mill massing of the molten polymer. In contrast to silicon dioxide, which showed no antioxidant effectiveness at 140°C., the pyrogallol complex gave an induction period of 50 hr. and the catechol complex, 105 hr. As shown in Figure 1, the temperature effect with these complexes is similar to that of carbon black. In each instance the relationship between log of the induction period and $1/T$ diverges from linearity near the polymer melting range.

These data support the conclusion that functional groups on the carbon surface are responsible for antioxidant effectiveness. Attaching similar reactive groups to the surface of silicon dioxide produces an effective antioxidant. Furthermore, the effect of temperature on the oxidative stability of polyethylene inhibited with these complexes is similar to that observed when carbon black is the anti-

oxidant. The nonlinear temperature dependence is consistent with the proposal that the average distance which a propagating radical must travel to be terminated on the carbon surface is much greater in the melt than in a solid, semicrystalline polymer.

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The Gelation Point of Alkyd Resins

The paper by M. Jonason on this subject¹ deals with a special case of the calculation of gelation points in condensation polymerizations, where reacting groups of a given species (as, e.g., hydroxyl, carboxyl, amino) do not all react at the same rate.

This general problem was solved in 1957 by Case.² The results of Jonason do not seem to agree with those of Case. The analysis can also be carried further than has been done by either of these workers.

If an anhydride A-B reacts with a triol C, the condition of gelation, in Case's notation is

$$2\beta 2\gamma / (\alpha + \beta) = 1$$

where α , β , γ are the fractions of A, B, and C groups reacted, the A group reacting first.

The result given by Jonason, by simplification of his eq. (12) is

$$2\alpha\beta 2\gamma / (\alpha + \beta) = 1$$

which is the result obtained by Case for the reaction of an unsymmetrical acid A-B with a triol C.

The discrepancy arises because Jonason has not distinguished between the anhydride and acid cases. In the former the anhydride group (A) must react first, before a B group can react, and this alters the statistical considerations.

For alkyd resins based on phthalic anhydride, reaction to the half-ester is in fact so rapid that α can be taken as unity. The two formulas will hence give the same numerical result for such polymers; but this is not general.

The discussion by Jonason of the reactivity of carboxyl groups calls for comment. An extreme reluctance of aromatic carboxyls to react is inferred from some results on