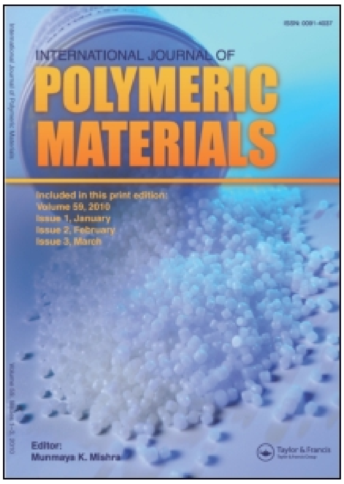

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Aharoni, Shaul M.(2001) 'How to Make Colorless Poly(ethylene terephthalate)(PET)', International Journal of Polymeric Materials, 48: 4, 425 — 445

To link to this Article: DOI: 10.1080/00914030108048840

URL: http://dx.doi.org/10.1080/00914030108048840

Intern. J. Polymeric Mater., 2001, Vol. 48, pp. 425-445
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How to Make Colorless Poly(ethylene terephthalate) (PET)

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(Received 10 November 1999; In final form 18 November 1999)

The methods and flow charts used for the industrial preparation of PET are shown and briefly discussed. Then, the three classes of contaminants usually appearing in PET are described and their causes elucidated. The organic contaminants impart to the produced PET an undesired yellow-amber tinge while those containing metal ions or elemental metals impart to the polymer various undesirable colors. Other organic contaminants are crosslinked gels and flakes, and especially the latter may cause filament rupture and may lead to the disruption of melt spin-draw processes. Some remedies to eliminate or minimize the appearance of such contaminants are then suggested, followed by a brief discussion of non-antimony catalysts which eliminate the gray discoloration usually imparted to PET by antimony-containing catalysts.

Keywords: Poly(ethylene terephthalate); Catalysts; Antimony; Gels; Industrial manufacture; Organic impurities; Discoloration

In the laboratory, poly(ethylene terephthalate) (PET) is usually prepared in two steps from dimethyl terephthalate (DMT) and ethylene glycol (EG) in glassware. The first step, transesterification:

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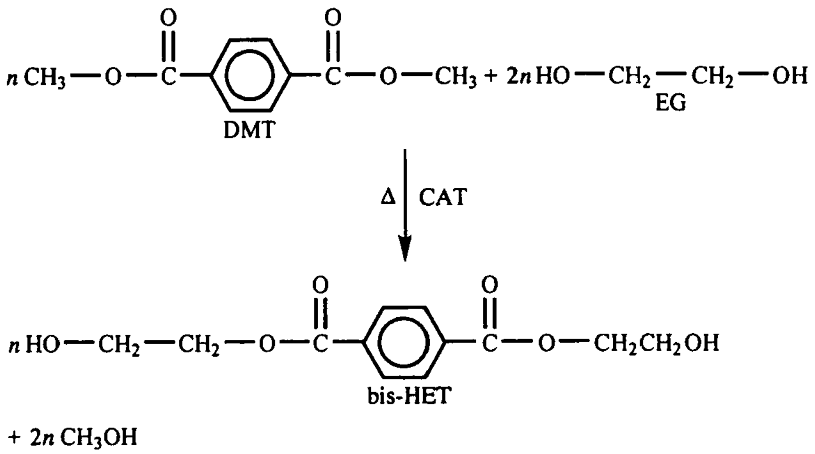
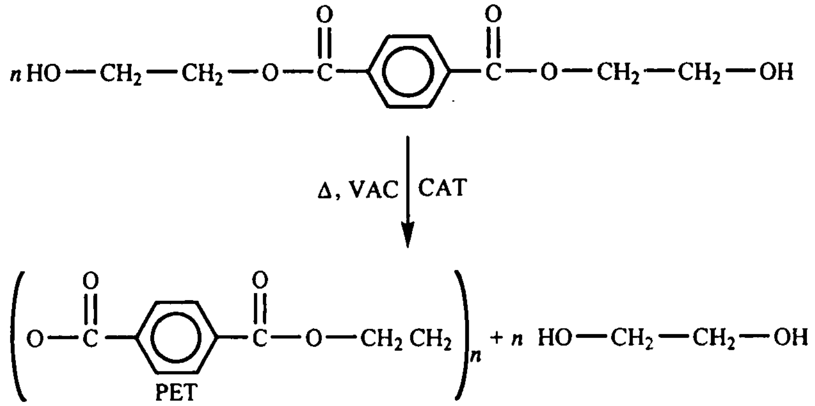


takes place under atmospheric pressure and the second step, polycondensation, proceeds under high vacuum:



Both steps may proceed in the absence of catalysts, but use them in order for the reactions to proceed at an acceptable rate.

In industry, there are two methods to produce PET. The first one is similar to the laboratory scale procedure, starting with DMT and EG and producing PET and the by-product methanol. In Figure 1 is shown a very simple scheme for this industrial process. The second industrial process starts with pure terephthalic acid (TPA) and EG. It, too, proceeds in two stages. In the first stage, TPA is reacted with a molar excess of EG under substantial pressure to form the major

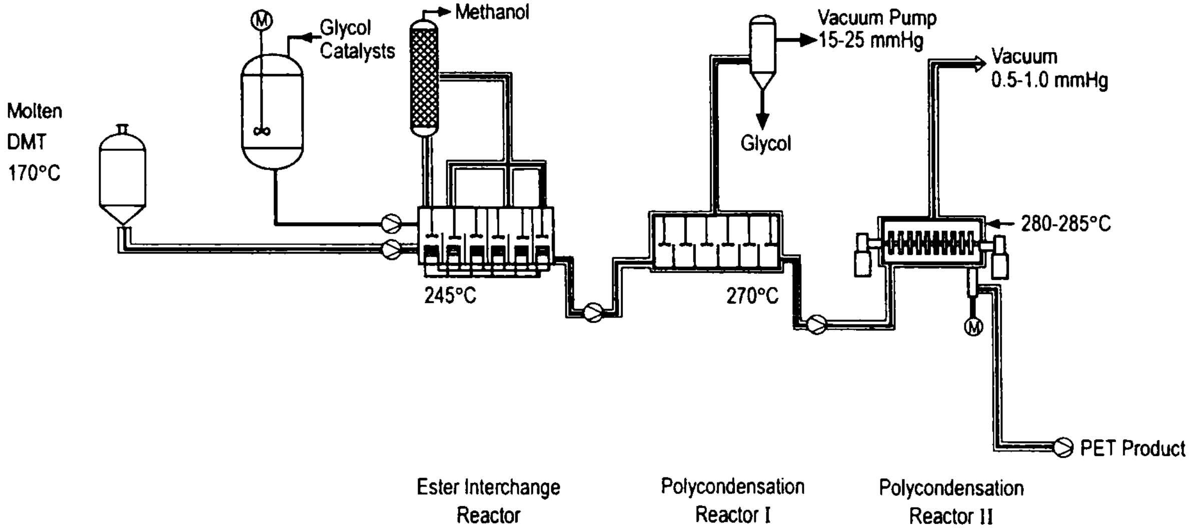
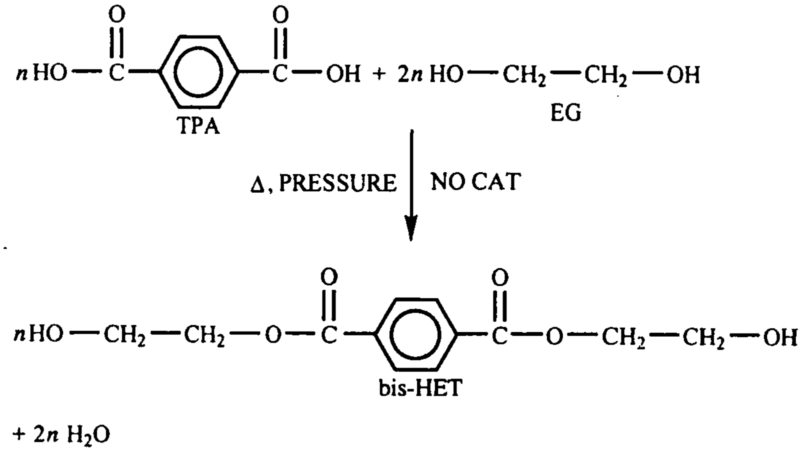
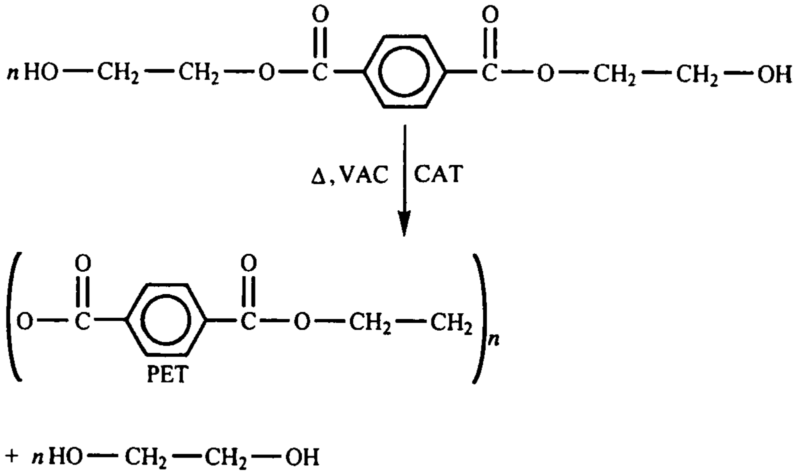


FIGURE 1 Simple flow chart for the industrial preparation of PET from DMT + EG.

intermediate product bis-hydroxyethylterephthalate (bis-HET), higher oligomers, and water:



The water is removed and the bis-HET and higher oligomers undergo a polycondensation process in several stages under increasingly high vacuum and temperature:



Unlike the case of DMT + EG, in the case of TPA + EG the initial step, of the esterification of TPA to form bis-HET, uses no external catalysts and only the polycondensation step is catalyzed. An almost childishly simple scheme of the industrial process of manufacturing PET from TPA and EG is shown in Figure 2.

In real life, away from academia, life is never as simple as in the laboratory or in Figures 1 and 2. A stripped down flow chart of a polymerization train for making PET from DMT and EG on industrial scale, is displayed in Figure 3. For simplicity and to minimize clutter, all electric and control circuitry are not shown in the figure. Notice the two series of reaction vessels, first transesterification followed by polycondensation, before one reaches the set of final polycondensation reactors, also called finishers. Note that the finishers each contains a set of large rotating flat discs. These are meant to greatly increase the surface area of the melt and decrease the thickness of the melt through which the evolving EG must diffuse, maximizing the rate of EG removal and molecular weight, M, buildup under the conditions of high temperature and very high vacuum existing in the finishers. In Figure 4 the stripped down flow chart of one industrial size polymerization train for making PET from TPA and EG is shown. Similar to Figure 3, all electric and control circuitry are not shown. Also not shown are the recycling pipes, valves and storage vessels through which the spent EG, containing substantial amounts of water, is recycled into the initial EG storage tanks.

Finally, in Figure 5 an industrial facility for solid-state polymerization of PET is shown. Such facilities are used in order to upgrade relatively cheap PET, whose intrinsic viscosity (I.V.) is about 0.65–0.70 dL/g, and increase its molecular weight and I.V. to ca. 1.0 dL/g. Such facilities are used when polymerization trains capable of creating PET with I.V. of ca. 1.0 are not available or in order to avoid the extended residence in the polymerization train, and the associated polymer degradation, required for M elevation from I.V. = 0.7 to I.V. = 1.0, and in instances where high purity recycled PET is available at the lower M which can be upgraded to a PET of higher M and substantially higher price.

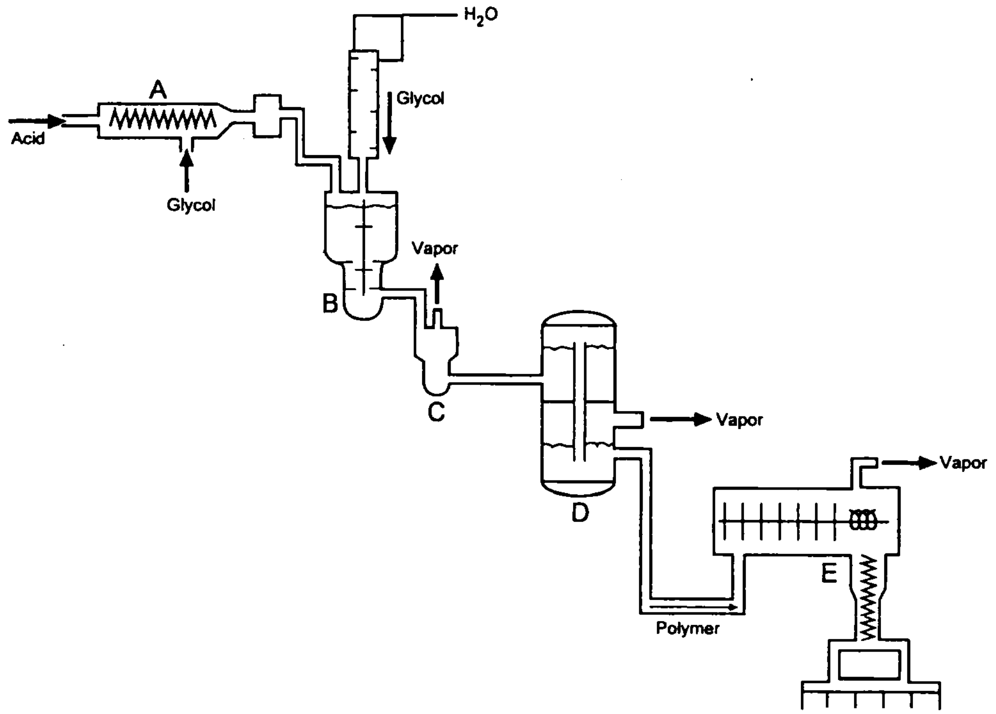


FIGURE 2 Simple flow chart for the industrial preparation of PET from TPA + EG.

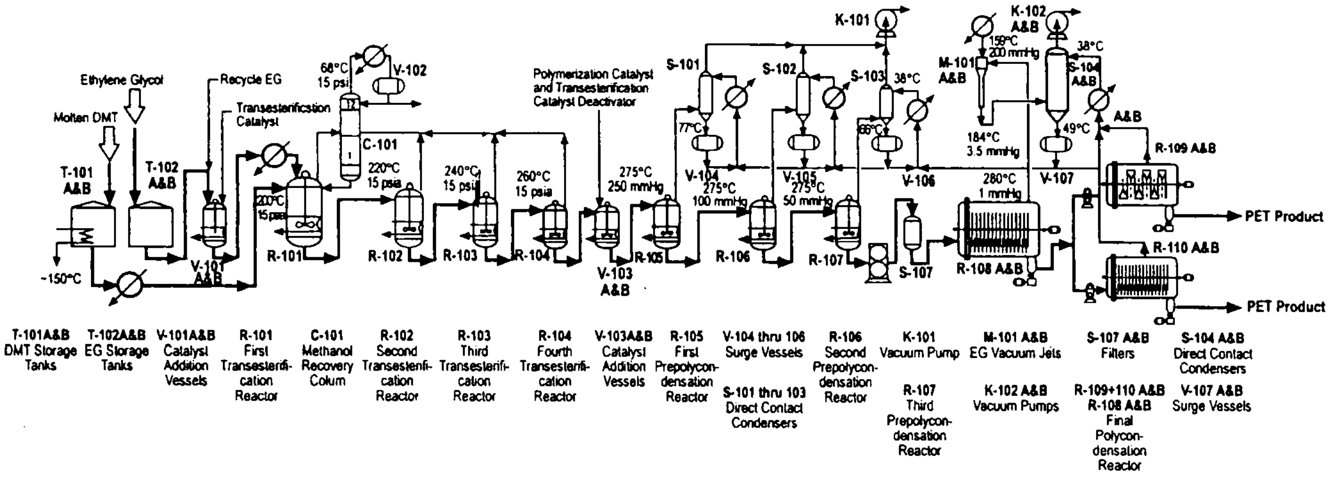


FIGURE 3 More realistic flow chart for the preparation of PET from DMT + EG.

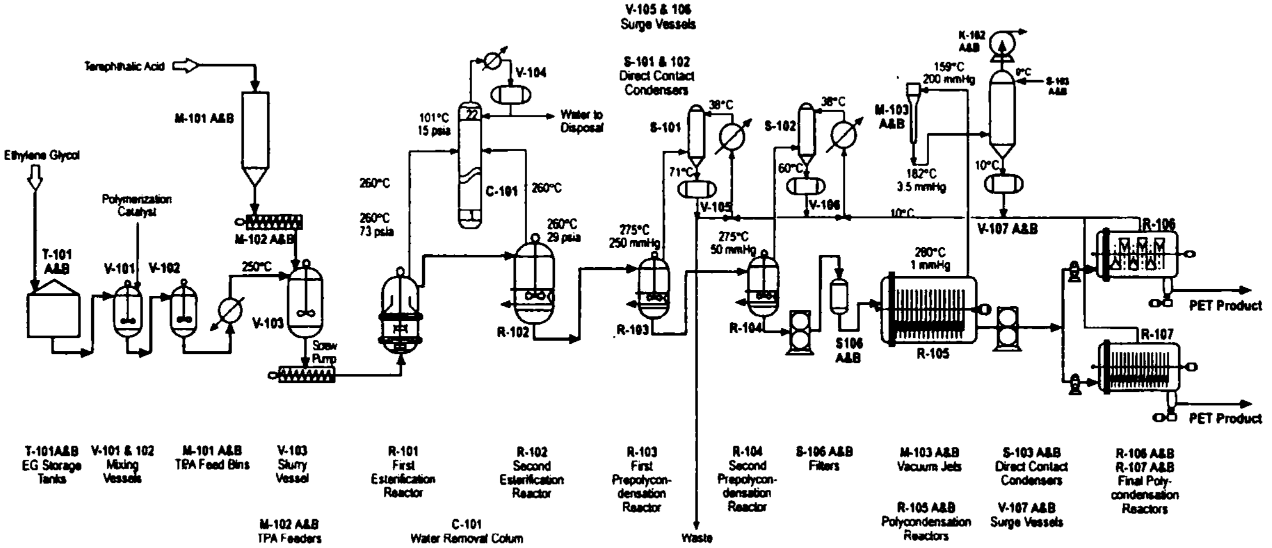


FIGURE 4 More realistic flow chart for the preparation of PET from TPA + EG.

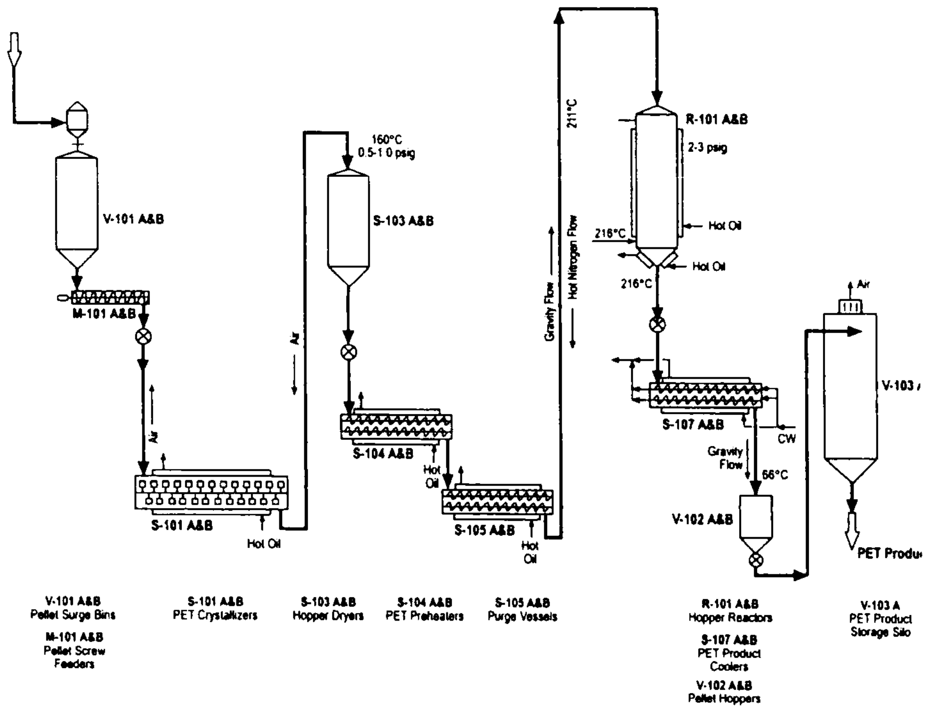
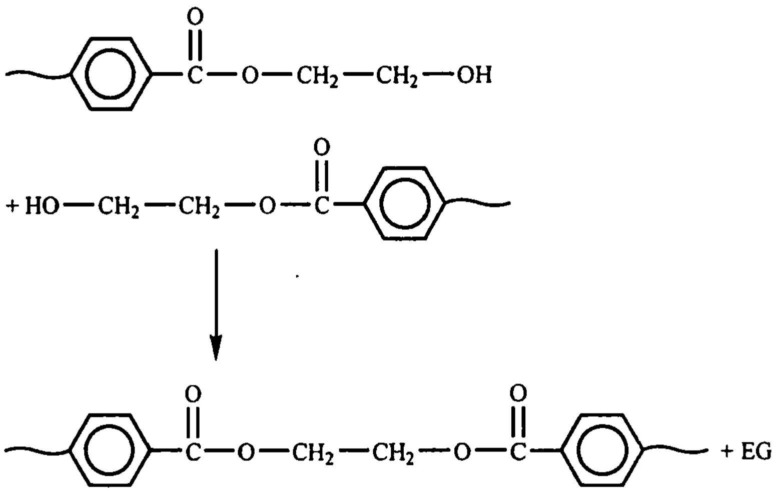
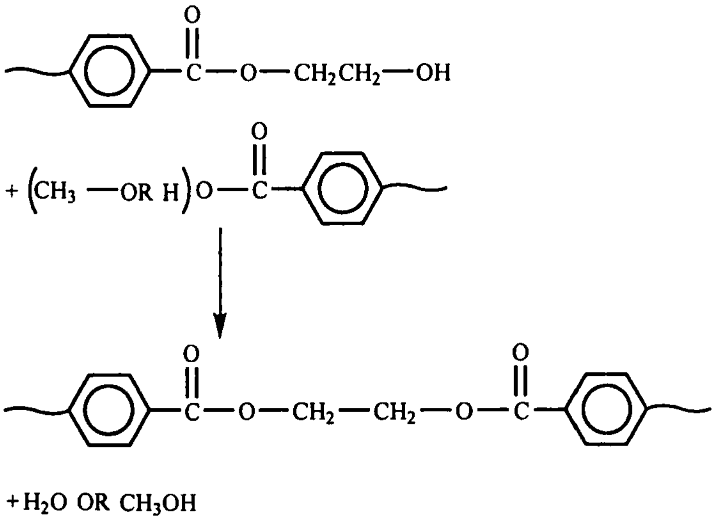


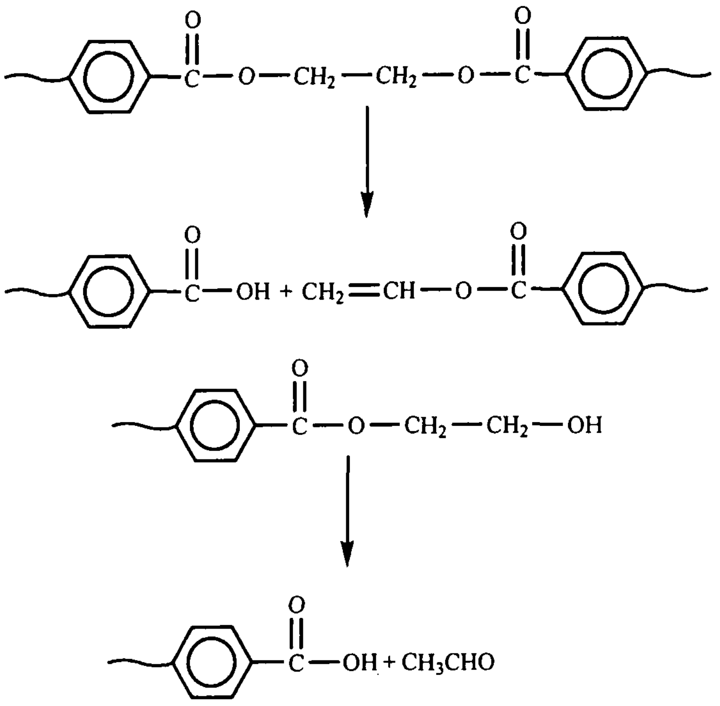
FIGURE 5 Flow chart for the solid state, molecular weight increase of PET.

During the polycondensation stage, some reactions contribute to overall chain growth:





While other reactions participate in the overall PET degradation process:



Additional reactions take place during the polycondensation stage, and to lesser extent during the esterification and/or transesterification stages. Among the important ones we may list the following ones:

$$\mathrm{HO{-}CH_2{-}CH_2{-}OH \longrightarrow HO{-}CH{=}CH_2 + H_2O}\ \text{(dehydration)}$$

$$\mathrm{HO{-}CH{=}CH_2 + 2O_2 \longrightarrow CO + CO_2 + 2H_2O}\ \text{(oxidation)}$$

$$\mathrm{HO{-}CH_2{-}CH_2{-}OH + 2O_2 \longrightarrow CO + CO_2 + 3H_2O}\ \text{(oxidation)}$$

$$\mathrm{HO{-}CH{=}CH_2 + HO{-}CH_2{-}CH_2{-}OH \longrightarrow}$$
$$\mathrm{HO{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}OH}\ \text{(dimerization)}$$

Although here they are shown in terms of individual monomers only, in reality monomers attached to chain-ends may undergo similar degradation reactions.

When all the reactions of polycondensation and degradation occurring concomitantly during the polymerization are taken together, they may be treated statistically as function of time to demonstrate

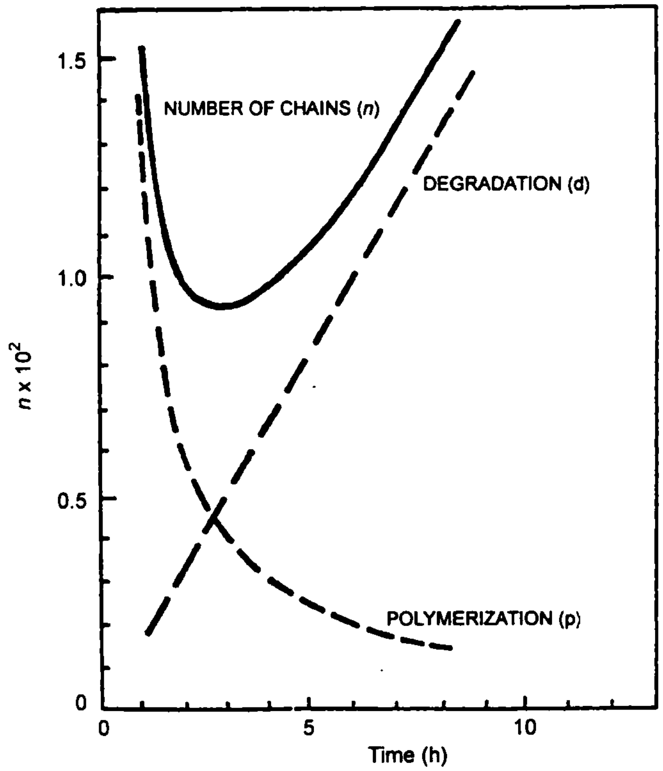


FIGURE 6 A p–d analysis of the polycondensation of bis-HET at 292°C.

the positive effects of polycondensation (p) and degradation (d). In Figure 6 is shown the p–d analysis of the conversion of bis-HET to PET at 292°C. The minimum of the solid curve reflects the point where the polymer reached its highest M and smallest number of chains. Earlier, the chain lengths is still growing, and later, degradation processes kick in to decrease the chain length and increase the number of shorter chains. With increased degradation, the PET shows a tendency to intensify its color, from the desired colorless or pure white, through straw color, to light and then amber color, and finally to deepening shades with increasing intensities of brown. In addition to discoloration, there are other kinds of undesirable contaminants usually present in industrially manufactured PET. Below, we shall discuss them using PET made from TPA + EG as an example.

There are three major classes of contaminants in PET that tend to discolor the polymer, affect its properties in a deleterious fashion, and/or disrupt its production and processing, especially the processes of melt spinning and drawing of fibers as they relate to very fine filaments or to highly drawn industrial-use multi-filament fibers. One class of contaminants are those created by chemical degradation reactions at the growing chain-ends or modifications of unattached monomers. Several of these reactions were shown above. The products of these reactions may continue and react with similar moieties, with other normal chain ends or with other monomers to form more complex structures that may contain multiple double bonds and produce increasingly intense "yellowing". Such complex organic structures may be attached to the PET chain, or remain unattached. Given time and temperature, they will continue to react and grow, to increase in complexity, and to intensify in color. Because of their size, they will remain soluble in the molten, and upon cooling in the vitreous polymer, imparting to it an undesirable color.

A second class of contaminants is also organic in nature, but appears not so much as chemical chain alteration or modifications but as physical contaminants: high-M yet low crosslinked gels, which are colorless or light in color, and highly colored highly crosslinked rigid flakes, of indeterminable molecular weight. Both gels and flakes are insoluble in common PET solvents, such as tetrachloroethane/phenol mixtures, but the gels greatly swell in these solvents and are generally of no defined shape. The flakes, however, are generally flat and polygonal with sharp angles between their facets. They look like the cracked mud polygons appearing on the surfaces of mud flats upon drying, and their size may be as large as a centimeter or more on each side. Both gels and flakes may be caused by either or a combination of any of the following three reasons: (1) *Oxygen* which may be entrained in the monomer feed but more frequently enters the polymerization train through air leaks at the axles of rotating parts, such as the discs in the finishers, through leaks at various entrance or exit portholes, through welding seams, or vents, *etc.* (2) *Melt flow irregularities* which result in the formation of localized melt pools with eddy currents instead of the desired plug flow. When the temperature in these localized quiescent pools is too hot or too low, uncontrolled polymer chain growth and crosslinking may take place.

In other words, gel formation may occur. When a hot-spot is present, intensive crosslinking and discoloration often accompany the gel formation. If a cold-spot is present, then the polymer may locally crystallize and chain growth will continue under conditions similar to those present during "solid stating". (3) Thin *static layers of molten polymer* coating surfaces of reaction vessels and transfer lines, especially on the flat rotating discs in the polymerization finishers. My experience have taught me that it is the gels and the more rigid flakes, often broken into sub-millimeter particles, which are the culprits in most instances of filament breaking during melt spin-draw operations, or worse, when so many of them are broken at the same time that dripping and drooling at the spinnerettes takes place and the spin-draw process must be interrupted in order to clean the polymerization train and transfer lines prior to re-start.

All these problems are, at least theoretically, preventable by better plant design, tighter production controls such as minimization of temperature fluctuations, and timely and careful maintenance operations. These, however, often conflict with plant cost, production targets, scheduling, *etc.*

The third class of contaminants are metal-containing colored species arising either from catalysts residues and degradation products, or from trace impurities in the monomer feed. Trace impurities may enter the system as ppm concentrations in the TPA monomer: elements such as Fe, Co, Mo, Ni, Ti, Cr, Ca, Al, Mg, Na and K in concentration of 1 ppm each or lower may come from the catalysts and their support used in the oxidation of para-xylene to TPA, and organic impurities may arise from incomplete oxidation of the precursor to TPA. Although important, these are not the major inorganic metal-containing species. The distinction of being the most undesirable metal-containing colored contaminants rests with leftover catalysts and/or their degradation products which remain entrained in the molten PET. At present, the grey discoloration imparted to PET by the degradation products of antimony-based catalysts is considered to be the least desirable, surpassing the yellowness imparted to PET by titanium-based catalysts currently available in the market and the blue-pink hue caused by cobalt salts.

As was described in detail in a previous article on this subject [1], in the presence of the large excess of EG in the polymerization train, all Sb-containing catalysts convert to antimony glycolate/glycoxide which exist in dynamic equilibrium with antimony trioxide. The Sb_2O_3 may arise from interactions of the catalyst or the Sb-glycolate/glycoxide with water in the system. In the same article [1], it was also shown that EG decomposes, rapidly in the presence of air and slowly in the absence of it, to water, carbon monoxide and carbon dioxide. At temperatures higher than ca. 215°C, species containing the Sb^{+3} ions and capable to, directly or indirectly, supply oxygen to the reaction, react with the carbon monoxide in a redox reaction to oxidize the carbon monoxide to carbon dioxide and to reduce the Sb^{+3} ions to elemental antimony. Figure 7 shows typical gas

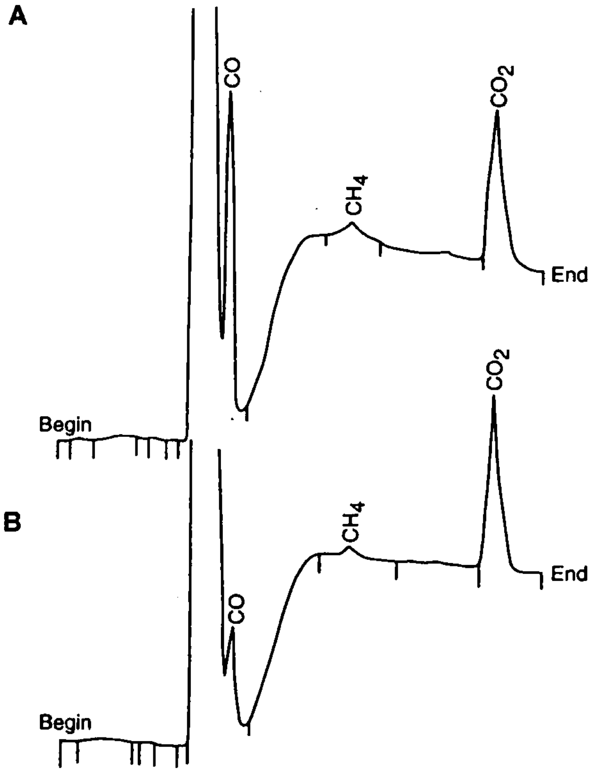


FIGURE 7 Gas chromatography of the head-space gases from the oxidative decomposition of EG at 225°C in the absence (A) and presence (B) of antimony-based catalyst. The same results were obtained from the reactions of EG with TPA or DMT.

chromatograms of the gasses in the reaction head-space. In Figure 7A a chromatogram obtained at about 225°C from a TPA + EG polymerization run in the absence of any catalyst indicates that the amount of carbon monoxide and carbon dioxide in the system were about equal. Figure 7B indicates that in the presence of antimony catalyst, most of the carbon monoxide was oxidized to carbon dioxide. Essentially identical results were obtained from ethylene glycol heated in the absence of TPA with and without Sb-catalysts, and even upon heating the catalyst antimony glycoxide all by itself. In all cases where carbon monoxide was oxidized to carbon dioxide, there appeared black particles identified as elemental Sb in the system. The relationships between reaction temperature, ratio of CO_2 to CO in the head-space, and color of the liquid or solid reaction mixture, are shown in Figure 8.

There are two important points that must be discussed at this junction. One is the fact that during common industrial polymerization of TPA + EG to PET, the antimony-based catalysts commonly used are antimony trioxide, antimony acetate, and rather rarely antimony glycoxide. The Sb-catalyst is usually charged with the EG in concentrations falling in the range of 300 – 400 ppm antimony/TPA. From this, only about 15% are reduced to the black elemental antimony, while the rest remain in the polymer as the white antimony oxide or antimony phosphate (the latter is a consequence of the use of phosphoric acid as an additive during the polymerization). The second important point is the fact that the elemental antimony usually appears as very small primary particles whose size in the order of 10 – 20 nanometers (see Fig. 9). Unless agglomerated together to form much larger aggregates, the small primary particles of elemental antimony are too small to disrupt the flow of molten polymer to and through the spinnerette and interfere with smooth spin-drawing process. Therefore, although they impart an undesirable gray tinge to the PET, the black primary Sb particles do not, by themselves, pose any danger to the continuous spin-drawing operation, and do not affect the frequency of filament rupture. Because of this, element analysis of "good" filaments and "bad" filaments shows no difference in the concentration of antimony. Moreover, even when only the immediate neighborhoods of ruptures in filaments were analyzed, the concentration of antimony right at the ruptures was

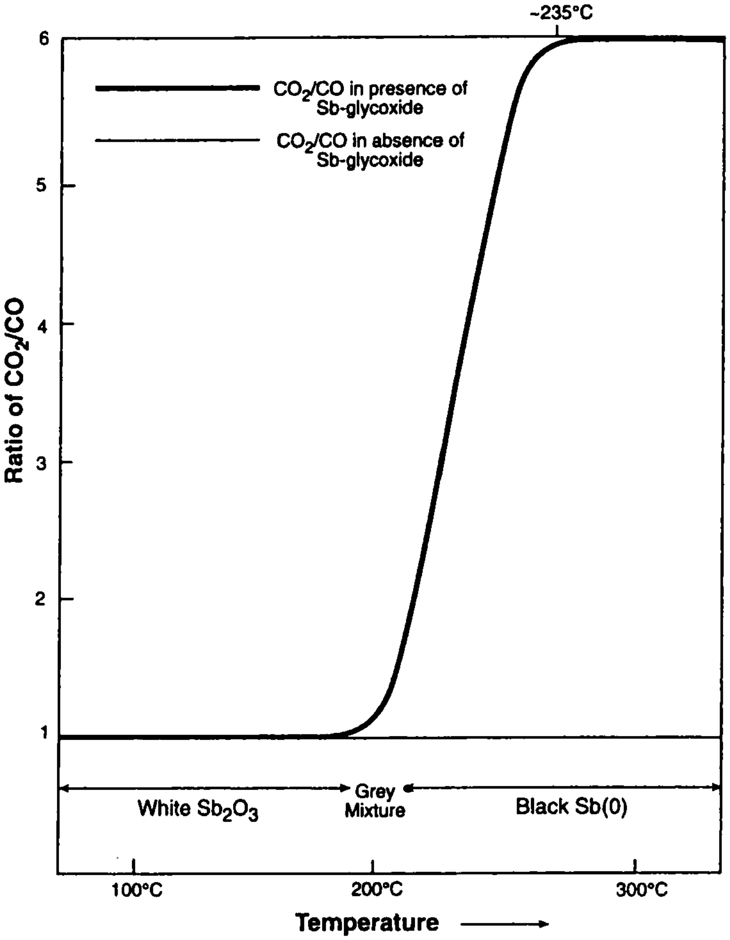


FIGURE 8 Relationships between temperature, CO_2/CO ratio, and product color in presence or absence to antimony-catalyst.

found to be typical of the whole PET bobbin and not measurably different.

One can make completely colorless PET by using either no catalyst at all, or using germanium dioxide as catalyst. In both instances the polycondensation proceeds very slowly and only modest M is obtained. The polymer, however, is of remarkable whiteness.

In order to come up with better catalysts, many elements were tested in many different compounds with respect to their catalytic

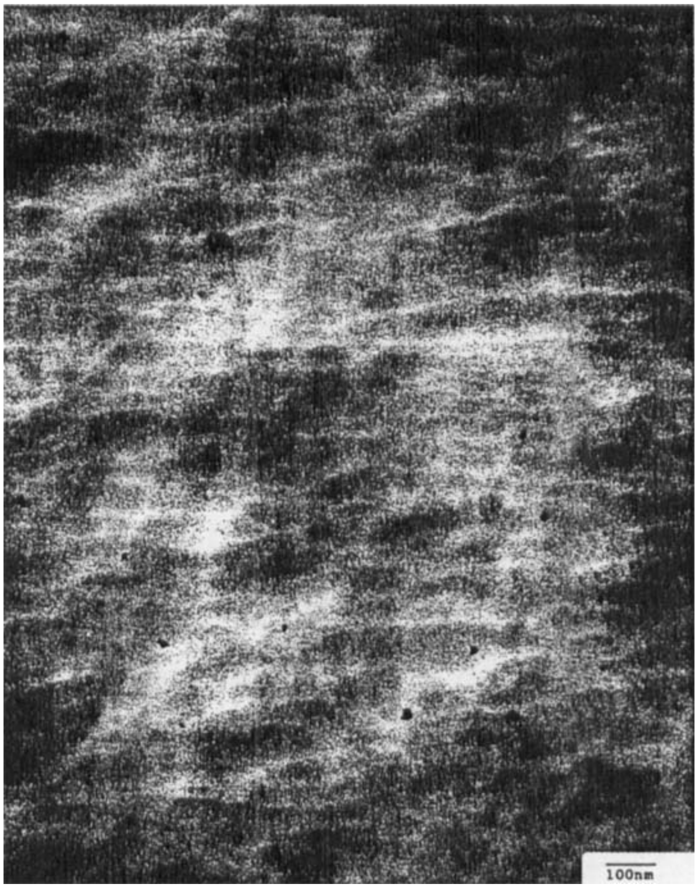


FIGURE 9 Electron micrograph of PET containing primary elemental antimony particles. Original magnification: 75000 X.

efficacy. A literature survey covering over 2000 references was conducted by me and the results are shown in Figure 10 in the form of the Periodic Table of the Elements. In it, the elements evaluated as catalysts for diacid (or diester) and diol polyesterification (as in the case of PET) are shaded, and the elements evaluated as catalysts for ring-opening polyesterifications (as in polylactone) are hatched. Many of the elements were evaluated for both and are, hence, both shaded and hatched. Among the important variables studied were the rate of polymerization and depolymerization, the

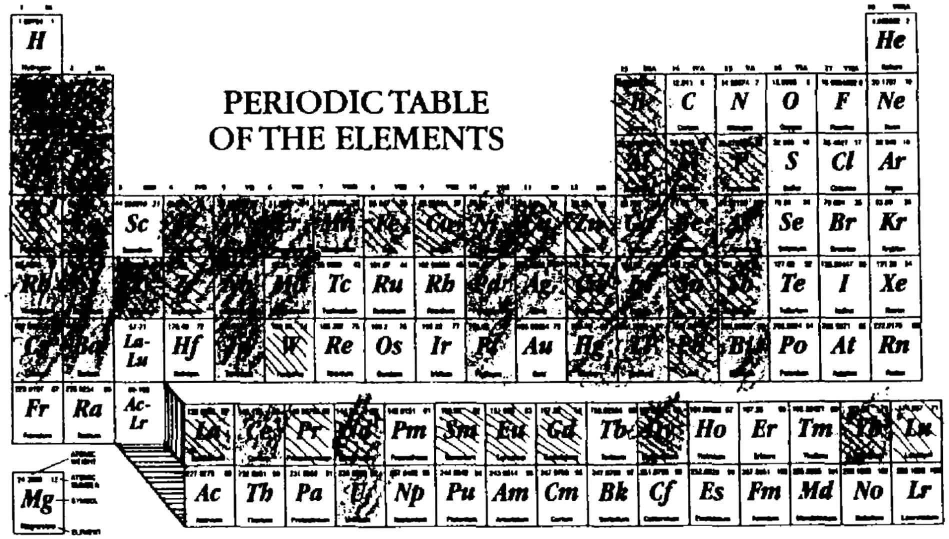


FIGURE 10 Periodic Table of the Elements in which elements tested as catalysts for diacid and diol polyesterification are shaded, and those tested for ring-opening polyesterifications are hatched.

necessary amount of catalyst, the stability of the catalyst, the color it imparts to the polymer, and other variables including cost. Based on my observations, a new family of polycondensation catalysts was invented by Aharoni and Goranov [2] and is now undergoing evaluation and development in the laboratories of the Specialty Chemicals Division of AlliedSignal Inc. These catalysts do not contain any antimony and the amount of titanium in them is sufficiently low not to impart yellowness to the PET product. On the other side, these catalysts are far more effective than antimony, operating at 50 ppm concentrations, are rather stable in water, and are highly soluble in the EG feed and in the reaction mixture even at ambient temperature. Typical polymerization results obtained from several of these polymers are shown in the Table below, together with the results obtained from titanium catalysts and antimony acetate under similar polymerization temperature and vacuum conditions.

In conclusion: There are 3 classes of contaminants existing in industrially prepared PET. One is the yellow-amber-brown colored products of chemical side-reactions; The second is organic colorless gels and amber-brown flakes; And the third is catalyst decomposition products, usually black elemental antimony that imparts gray coloration to the polymer. The gels and, especially, flakes are responsible for most filament ruptures and spin-draw process inter-

TABLE PET polymerizations using acidic glycolate/glycoxide catalysts, and comparative examples[a]

Test	*Catalyst code*	*Catalyst description*	*Intrinsic viscosity I.V. (dl/g)*	*Minutes in vacuum*
1	CATALYST 5	Ti only, pH = 0–1	0.88	150
2	CATALYST 2	3:2:1 Ti/Zr/Ge; pH = 0–1	0.94	150
3	CATALYST 1	3:2:1 Ti/Zr/Si; pH = 0–1	0.95	135
4	CATALYST 3	1:1:1 Ti/Al/Zr; pH = 0–1	0.89	125
5	CATALYST 4	1.275:1:1 Ti/Mn/Zr; pH = 0–1	0.86	120
6	CATALYST 10	5:4:1 Zr/Ti/Ge gel; pH = 5–6	0.85	150
7	Tyzor TE	Ti only	0.84	135
8	CATALYST 11	8:1 Al/Co; pH = 0–1	0.65	180
9	Control	antimony acetate	0.92	180

[a] All catalysts except for antimony, are at 50 ppm concentration. Antimony acetate is at 400 ppm concentration. All other reaction conditions are identical.

ruptions. The first two classes of contaminants may be eliminated or minimized by prevention of oxygen leaks into the polymerization train, by better design to eliminate quiescent melt puddles, hot spots and/or cold spots, and minimization of the formation of layers of molten polymer stuck in more or less permanent fashion onto the internal surfaces of the reaction vessels and transfer lines. The last class of contaminants, containing the free elements or metal-ions, are typified by antimony-based catalysts. In order to eliminate or minimize the gray discoloration, the Sb-catalysts may be completely replaced by others, or the amount of Sb-catalyst substantially reduced and other, more efficient and less-coloring catalysts added instead.

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[1] Aharoni, S. M. (1998). *Polym. Eng. Sci.*, **38**, 1039.
[2] Aharoni, S. M. and Goranov, K. N., U.S. Provisional Patent Application No. 60/077, 083 of March 6, 1998.