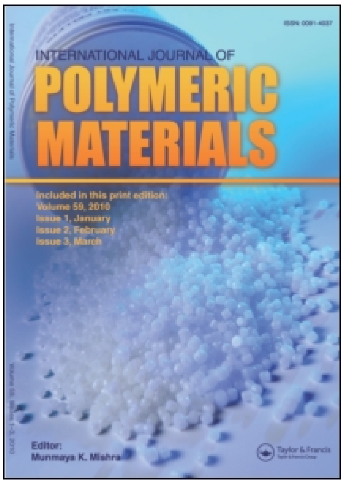

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The Current Status of Catalysis and Catalyst Development for the Industrial Process of Poly(ethylene terephthalate) Polycondensation

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In this survey of the industry, it is shown that despite the partial dissatisfaction with antimony-based polycondensation catalysts these catalysts are expected to remain the mainstay of industrial PET polycondensation catalysis. This is despite the intensive efforts invested in the search of other, stable and inexpensive non-antimony catalysts, such as those based on titanium, aluminium, and several transition metals such as molybdenum, cobalt and zirconium.

Keywords: Poly(ethylene terephthalate); PET; Polycondensation; Catalysis; Antimony; Titanium

INTRODUCTION

Since the first polyester patents of H. W. Carothers, P. Schlack, J. R. Winfield and J. T. Dickson, who provided the basic knowledge of our current industrial polyester process, there were many polymer scientists trying to develop new catalysts. The metal catalysts based on antimony and germanium dominate the industrial production

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*e-mail: drthiele@polyester-technology.com process since that time. Meanwhile nearly all elements of the periodic system have been tried as catalysts in the polyester polycondensation. The main driving force of catalyst research during the 1950–1970 period was to protect or circumvent existing polyester process patents. The scientific work at that time was concentrated in describing the catalytic mechanism of the metal catalysts [1–6]. A large number of metals and nonmetals show a significant catalytic effect but the replacement of antimony and germanium as polycondensation catalysts in an industrial scale has not succeeded until today. Between 1970 and 1990 the main emphasis of the development work was the optimisation of the catalyst recipe, feeding and preparation techniques and polymer stabilization to meet the requirements of polyester processing such as spinning and film making. With the fast growing packaging industry where PET is used to make bottles and other packages, a new wave of catalyst development was observed starting in 1990. The main target of this still ongoing development is on one hand the replacement of the antimony which will be shown below to have a negative environmental impact, and, on the other hand, the replacement of germanium because of its incredibly high price. Besides, until today there is no scientific evidence regarding any negative health impact of antimony used as polycondensation catalyst and no governmental regulation of the many companies searching for new catalytic systems. It seems that the new generation of chemists like in general idea of replacing antimony by a more powerful and efficient catalyst. The aim of this paper is to give an overview about the industrial catalyst knowledge, the driving forces for new developments and a summary of the recent catalyst patents.

THE CURRENT INDUSTRIAL CATALYST KNOWLEDGE

Antimony

Today, three different antimony compounds are used as polycondensation catalysts. The majority of the polyester is catalyzed by antimony trioxide originating from a wide variety of sources. More than 12 companies are competing in this market. Antimony triactate which is produced by a few companies is used for about 30% of the total polyester production. As a niche product also the highly purified antimony glycolate/glycoxide is in some cases applied. Important for the success for all this commercial antimony catalysts is the correlation between price and product performance. Because of the current highly increased line capacity of continuous plants, up to 400 t/d and more, the catalyst business functions in a very sensitive network of experience and trust. In addition to the kind and source of the antimony catalysts, the preparation and feeding technology play a major role regarding the final product quality. Comparing the basic quality and performance data of polyester, like color, clarity, DEG-content, COOH-groups, filterability and spinnability out of well optimized and operated plants, one can find no significant quality differences between polyester polymers catalyzed by oxide, acetate or glycolate of antimony.

Germanium

Germanium catalyzed polyester were mainly used during the early years in film applications because of its high clarity. Today the main portion of germanium catalyst is still consumed by Japanese polyester producers who like the high brilliancy of the polymer for bottle applications. Because of its tendency to support the oxidative degradation germanium catalysts are used together with stabilizer based on phosphorus. Germanium is applied as germanium dioxide whereas the main issue is to provide an oxide with high solubility. Meanwhile catalyst producers who specialize in germanium catalysts are offering stable solutions of germanium dioxide. The price of about 500 US$ per kg pure germanium dioxide is the main driving force to gradually replace this catalyst.

Recent Catalyst Developments

With the booming growth of the polyester bottle resin production during the late 1980's and the early 1990's the development of antimony free catalyst systems was supported by different driving forces and ideas. One driving force was the sometimes hysteric discussion of environmental issues in the public, which scared the polyester producers lest they be subjected to public pressure.

TABLE I Improvable properties of antimony-based catalysts

Property	*Effect to product or processor*
1. Catalytic efficiency	150–300 ppm Sb depending on equipment and technology, delta IV 0,15–0,25 dl/g per hour
2. Precipitation and discoloration	Sb metal as fine black particles, Sb-oxidhydrates, insoluble $Sb2O5$, $SbPO4$ and other Sb-P species
3. Reaction products of antimony	Sb-oligomers occurring as spinning smoke deposited as "egg shells" around spinnerets

Another driving force was the always present desire to improve the reactivity. It is still the target today to have a catalyst system which is able to increase the plant capacity significantly and which provides the same or better product quality obtained from antimony.

Development Targets for New PET Catalysts

To define development targets for a new catalyst the properties of antimony witch could be improved are collected in Table I.

The catalytic efficiency is related to the polymer quality: the less catalyst – the higher the purity of the polyester in general, and related to production cost: the less catalyst – the lower its cost. As one can see, major points are precipitation and discoloration. This is associated with a variety of secondary effects such a black spots created by antimony metal deposits at pipe and reactor walls, greenish to grayish color tone and white to gray haziness of the polymer. Also the crystallization rate and level of polyester is significantly influenced by the kind and concentration of catalyst [7]. So it was found that Ti-catalysts provide a low crystallization rate [8]. One important process impact of antimony is caused by the reaction of oxygen with glycol or glycolates during esterification and prepolycondensation followed by the creation of CO which reduces the Sb+3 present in the reaction mixture to metallic grayish precipitation [9]. Out of this collection one can summarize the following development targets for a new polyester catalyst:

→ Higher catalyst efficiency, high reaction speed in melt phase and solid phase polycondensation, low catalyst concentration, low catalyst cost.

- → High polymer purity reflected in brilliancy, white color, high transparency, excellent polymer filterability, low oligomer content.
- → High thermal and oxidative polymer stability, low acetaldehyde generation.
- → Non toxic, environmentally neutral, easy handling and easy application.
- → Added values such as catalytic activity during esterification, process functional like improved IR absorption or significantly changed crystallinity.
- → No negative impact to downstream processing like spinning, bottle blowing or film making.

Titanium

Titanium alkoxides are the state of the art catalysts to produce poly(butyleneterephthalate) (PBT). Until today simple Ti-alkoxides play no role as catalysts for the production of PET. Because of their high catalytic activity titanium catalysts are the basis of most new developments concentrated on modification of titanium catalysts to find new formulations which fit the above mentioned development targets. The well-known negative properties of simple Ti-alkoxides are the yellow discoloration, the precipitation of TiO_2 by hydrolysis connected with low reproducibility of the catalytic activity and the thermal instability of the polyester. To reach a neutral color tone, titanium is mostly combined with cobalt [10, 11] or with an organic blue toner [12]. Additionally phosphorus compounds are used to improve the thermal stability. To prevent against an early catalyst destruction by hydrolysis different strategies are applied. One path is the creation of stable Ti-complexes by adding before or during the reaction complexation compounds like 2-hydroxy carboxylic acid such as citric acid or tartaric acid [13, 14] or α-hydroxy-ketones like α-tropolone [15]. Another way is the application of finely dispersed Ti-oxides/hydroxides or mixed Si/Ti precipitate which becomes partially resolved under the polycondensation conditions. Here, the idea is to preserve a certain solubility of the solid precipitate and use the precipitate particles as Ti-donor during the whole polycondensation reaction [16–18]. Another approach to preventing the discoloration and providing a stable catalytic Ti-complex is the composition of phosphinic acid titanates that are combined with phosphoric acid [19]. Advantages are high catalytic activity at low catalyst content, high clarity and low discoloration.

To protect the catalyst metal like titanium against hydrolysis during the process a new principle is suggest by absorbing the catalyst before the reaction at the inner surface of finely dispersed charcoal or silica [20]. To prepare a polymer of high clarity and brilliancy with such kind of semi soluble catalyst the particle size must be significantly less than 500 nm.

Because of the high catalytic activity of titanium and the possible acceleration of the esterification reaction, too, titanium will remain one of the main tools for developing new catalyst systems.

Aluminum and Zeolites

During the last decade catalysts based on aluminum came into the focus of the technical development. The first patents suggesting aluminum as catalyst date back to the 1950's [21]. Zeolites have been used 25 years ago as finely distributed additives to modify film polyester [22]. It might be a matter of practical experience that shortly before the mentioned additive patent expired, the catalytic activity of zeolites was discovered. The minimum zeolite concentration useful to get a sufficient polycondensation reaction was reported as 900 ppm. The commercial zeolites recommended for use as catalysts are dried and contain 1,5–2,5% water [23]. It was later discovered that the drying of the zeolites after their synthesis provides lower catalytic activity compared to zeolites commercially available with their original water content of approx. 30 weight %. The amount of aluminum dissolved in the reaction mass of the polycondensation was found to be the catalytic active component. The sufficient concentration of these semi soluble zeolites could be reduced to 400 ppm. Color and thermal stability are adjusted by the addition of small amounts of cobalt and phosphorus compounds [24]. Finally a combination of aluminum trichloride and glycol soluble cobalt compounds like cobalt acetate is suggested as polycondensation catalyst using 15 ppm Co and 55 ppm Al [25].

SUMMARY

Beside titanium and aluminum only a few other elements and element combinations like samarium [26], tin [27], iron [28], molybdenum and tungsten [29], magnesium/potassium/phosphorus [30] and zirconium/silicon/cobalt [31] have been suggested as polycondensation catalysts during the last decade. Until today there is no commercial substitute to antimony in sight, even though some of the described development catalysts were tried on an industrial scale and are also available in semi commercial amount. The risk to change the catalyst of a large continuously running polyester plant is high because of the very close connection between kind of catalyst and the downstream processing performance in textile and bottle processing. Therefore we may see a prolonged development phase until one could say that a new polyester catalyst was successfully introduced to the industry.

References

[1] Zimmermann, H. (1962). *Faserforsch. Textuiltechn.*, **13**, 481.
[2] Yoda, K. (1971). *Kogyou Kagaku Zasshi*, **74**, 1476.
[3] Rafler, G., Reinisch, G. and Bonatz, E. (1974). *Acta Chim. (Budapest)*, **81**, 253.
[4] Tomita, K. and Ida, H. (1975). *Polymer*, **16**, 185.
[5] Laserova, R. and Dimov, K. (1976). *Die Angewandte Makromolekulare Chemie*, **55**, 1.
[6] Rafler, G., Tesch, F. and Kunath, D. (1988). *Acta Polymerica*, **39**, 315.
[7] Gunther, G. and Zachmann, H. G. (1983). *Polymer*, **24**, 1008.
[8] Jabarin, S. A. (1987). *J. of Appl. Polym. Sci.*, **34**, 85.
[9] Aharoni, S. M. (1998). *Polym. Eng. Sci.*, **38**, 1039.
[10] Hagen, R., Schaaf, E. and Zimmermann, H., *Internation Patent Application PCT WO 96/37534*, 22 Mai, 1996, Karl Fischer Industrieanlagen GmbH.
[11] Dominiguez de Walter, L., Moore, B. B. and Klein, P., *European Patent Application EP 0 699 700 A2*; 17 August, 1995; Hoechst Aktiengesellschaft.
[12] Hilbert, S. D. and Davis, T. G., *US-Patent 5 744 571*; 15 October, 1996; Eastman Chemical Company.
[13] Peuker, I. *et al.*, *German Patent DD 286 174 A5*; 17 July, 1989; VEB Chemiefaserkombinat Schwarza.
[14] Naylor, C. C. *et al.*, *International Patent Application PCT WO 97/47675*, 4 June, 1997, Imperial Chemical Industries PLC.
[15] Rafler, G. *et al.*, *German Patent DE 195 37 365 C1*, 6 October 1995, Frauenhofer-Gesellschaft zur Förderung der angewandten Forschung e.V., 80636 München.
[16] Thiele, U. *et al.*, *German Patent DE 195 13 056 A1*, 7 April, 1995, Zimmer AG.
[17] Martl, M. *et al.*, *International Patent Application PCT WO 95/18839*; 7 January, 1994, Akzo Nobel N.V.
[18] Takeshi, O. *et al.*, *European Patent Application EP 1 013 692 A2*; 23 December, 1999, Mitsui Chemicals, Inc.
[19] Lustig, S. R. and Burch, R. R., *US-Patent 5 981 690*, 15 April, 1999.

[20] Thiele, U. *et al.*, *European Patent Application EP 1 031 590*; 27 February, 1999, Lurgi Zimmer AG.
[21] *US-Patent 2 711 402*; 21 June, 1955; Imperial Chemical Industries PLC.
[22] Anderson, J. C., *US-Patent*; 26 May, 1972; E. I. Du Pont de Nemours and Company.
[23] Jackson, R. C., *US-Patent*; 20 March, 1990; E. I. du Pont de Nemours and Company.
[24] Thiele, U., *US-Patent*; 24 December, 1996; Zimmer AG.
[25] Goodley, G. R., *International Patent Application PCT WO 96/41828*; 8 June, 1995; E. I. du Pont de Nemours and Company.
[26] Giampietro, N. *et al.*, *European Patent Application EP 0 626 406 A2*; 24 May, 1993; Enichem S.p.A.
[27] Larkin, W. A. *et al.*, *Europena Patent Application EP 0 419 254 B1*; 20 September, 1990; Elf Atochem North America, Inc.
[28] Nakashima, Takahiro *et al.* (2000). *Jpn. Kokai Tokkyo Koho JP 2000 119,382*; 9 October, 1998; Toyobo Co., Ldt., Japan; *CA Selects: Polyesters*, **12**(4), *CA 132*:***279664g***.
[29] Kasowski, R. V. and Burch, R. R. Jr., *US-Patent 5 382 650*; 20, December, 1993; E. I. du Pont de Nemours and Company.
[30] Hori, Hidechi *et al.* (2000). *Jpn. Kokai Tokkyo Koho JP 2000 159,873*; 22 September, 1998; Mitsubishi Petrochemical Industries, Co., Ltd., Japan; *CA Selects: Polyesters*, **15**(18), *CA 133*:***17993p***.
[31] Honda, Keisuke *et al.* (2000). *Jpn. Kokai Tokkyo Koho JP 2000 109,553*; 6 October, 1998; Toray Industries, Inc., Japan; *CA Selects: Polyesters*, **12**(4), *CA 132*:***279658h***.