

Chromic Titanate Catalysts for High-Melt-Index Polyethylene by the Particle-Form Process

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Synopsis

A novel thermal activation procedure for ethylene polymerization catalysts made from silica, a chromium compound, and a titanium ester greatly increases the melt index of the polyethylene product under commercial polymerization conditions in comparison with conventional air activation. The novel activation has two steps. The first is heating under a reducing gas atmosphere ($N_2 + CO$). The second step is partial oxidation at a lower temperature for a shorter time. The size of the melt index increase is related to the average oxidation number of the chromium, but oxidized chromium can be reduced and the effect persists with less intensity. Additionally, the magnitude of the effect is dependent upon gas flow rates during activation and prior chemical and thermal history of the chromium-silica combination. Since titanium is required for the two-step activation to be effective in increasing melt index, titanium atoms have a critical influence on the catalyst active sites. An experiment with tetraethoxysilane added to the catalyst shows that titanium and chromium atoms must be next nearest neighbors (separated by oxygen atoms).

INTRODUCTION

Polymerization of ethylene in slurry or particle form with thermally activated chromium on silica catalysts is an important commercial process with manufacturing plants in many parts of the world.^{1,2} The process has been very successful in the manufacture of polyethylene resins suitable for various uses. However, for a long time, the production of resins with melt index values of about 5 or higher has not been feasible within the temperature limits of the process. Research workers in the industry have searched for methods to remove this limitation in order to open up other application areas. Many patents have been issued with the preparation of high melt index particle form polyethylene as an object and with modification of chromium catalysts as the means.³⁻⁹

Although these inventions are successful in varying degree, there has been no scientific account of the procedure necessary to obtain high-melt-index products and the chemical and physical changes in the catalyst. This article describes the preparation procedures for one particular type of thermally activated catalyst described in U.S. Patent 4,041,224.¹⁰ Experiments which relate the melt index changes to chemical changes in the catalyst are also reported.

In our research efforts to find catalysts leading to higher melt index particle form polyethylene resins, chromium titanate catalysts were discovered.^{9,11} Further investigation of chromium titanate catalysts led to the discovery that changing the thermal activation procedure gave further large melt index increases. Thus, as shown by the patent,¹⁰ the catalyst of this article has two distinctions from the earlier chromium on silica catalysts.¹²

The first distinction is that a titanium compound must be added to the silica-chromium compound composition after removal of surface water, but prior to the heat activation.

The second distinction is in the heat activation procedure. While the conventional catalysts are heated in a bed fluidized by dry air, the procedure discovered to give high melt index is a two-step activation. The first step is heating in, preferably a mixture of, nitrogen and carbon monoxide. The second step is a lower-temperature air treatment for a relatively short time. Both steps are done with the catalyst fluidized by the gas required. Under otherwise similar conditions of polymerization, the increase in melt index is related to the air treatment temperature (Table I) and the titanium content of the catalyst (Table II). The melt index as a function of air treatment temperature has a broad flat maximum from 450 to 550°C, with a sharp drop-off to much lower values on either side. In the absence of titanium, there is no observable melt index increase even if the optimum two-step activation procedure is followed.

EXPERIMENTAL

Materials

Ethylene and isobutane were obtained from the Chemplex plant and passed through columns of copper catalysts and molecular sieves for removal of traces of oxygen and water. Air for catalyst treatments was Linde Dry Grade, and it was passed through columns of molecular sieves for additional drying. The N₂ used for catalyst activation and general purging was vaporized from a liquid reservoir and passed through columns of copper catalyst and molecular sieves.

Titanium tetraisopropoxide was obtained from Alfa Division of Ventron Corporation and was used as received. Tetraethoxysilane from Petrarch Systems, Inc., was also used as received. Davison Chemical Division grade 952 silica was a starting material for all catalysts. For some catalyst preparations it was

TABLE I
Effect of Catalyst Oxidation Temperature on Polyethylene Melt Index^a

Air treatment temperature, °C	Reactivity, g/g cat. h	Productivity, g/g cat.	Melt index
400	1167	1945	9.7
450	1852	2469	44.7
500	2484	2484	39.5
550	2227	2227	47.8
700	2150	2350	3.3

^a Data from U.S. Patent 4,041,224.¹⁰

TABLE II
Melt Index of Polyethylene at 5000 Productivity as Affected by Titanium Content

Ti, wt %	Ti/Cr, atomic ratio	Melt index
0.0	0	0.3
0.92	1.0	1.0
2.3	2.5	5.0
3.2	3.5	27.5
3.8	4.1	24.0
4.0	4.3	18.0

used as a mixture with 2 wt % chromium trioxide. For other preparations, it was combined with ammonium chromate and pinacol. Pinacol hydrate was obtained from Eastern Chemical Company. The ammonium chromate, chromium trioxide, and the reagents used for iodometric determination of oxidized chromium were normal reagent grades.

Polymerization Reactions

The method and equipment for the polymerization tests were the same as previously described.¹¹ Melt indices were determined by ASTM D-1238, Condition E. Since the yield of polyethylene per gram of catalyst can affect melt index with this type of catalyst, comparisons are made between resins of similar productivity.

Catalyst Preparations

Thermal activations were done in a quartz tube heated from the outside by a surrounding electric furnace. A coarse fritted disk fused to the tube served to support the fluidized bed. The inside diameter was 1 in. near the fritted disk, and the catalyst charge was 8.0 g. The temperature of the bed was measured by a thermocouple placed near the center. Gases used in the activations flowed upward through the disk, producing fluidization. Flow rates of the gases were measured by rotameters kept at room temperature. When a mixture of carbon monoxide and nitrogen was used for high-temperature activation, the gases were combined downstream from two rotameters. The volume percent of carbon monoxide was kept at 7% to have about a 100% safety factor in relation to the minimum flammability concentration if mixed with air.¹³

A. Catalysts with Postreduction Using Carbon Monoxide

A series of catalysts was prepared starting with 8.0 g of Davison grade 952 silica combined with 2 wt % CrO₃. The starting material was charged to the quartz tube and an N₂ flow of 300 mL/min was started. The temperature of the fluidized bed was raised to 170°C and was held for 1 hr. By means of a syringe and long needle, 2.1 mL titanium tetraisopropoxide was added dropwise. After about 10 min, CO was admitted to the N₂ stream at 21 mL/min. The temperature was increased linearly over several hours to 700°C and held for 5 h by an automatic programmer. The bed of catalyst was then adjusted to a desired air treatment temperature over a period of about 45 min. The flow of CO was stopped and pure N₂ was passed through the catalyst bed for 15 min to remove the CO. A flow of air at 300 mL/min was started and the N₂ stopped. After the air treatment, the N₂ flow was started again. The catalyst preparation was cooled to about 100°C under N₂ fluidization and then transferred to a storage flask without contact with room air.

Another series of catalysts was prepared in the same way, except that after the air treatment there was a reduction with pure CO. After the air treatment, the temperature was adjusted to 400°C while a flow of N₂ removed air from the catalyst bed and quartz tube. Then, CO was passed through the bed at 300 mL/min for 15 min. Each catalyst was then cooled in N₂ as before and transferred to a storage flask.

TABLE III
Polymerization Tests Showing Effect of Oxidized Chromium and Final Reduction on Melt Index

Air temp., °C	Air treatment time, min	Final reduction with CO at 400°C	Cr ⁶⁺ wt %	Cr ⁶⁺ % of total Cr	Melt index ^a
700	15	no	0.62	62	3.0
700	5	no	0.57	57	5.0
700	15	yes	0.00	0	0.29
600	15	no	N/A	N/A	12.9
550	15	no	0.48	48	48
550	15	yes	0.00	0	1.7
500	15	no	0.25	25	49
500	15	yes	0.00	0	7.6
450	15	no	0.305	30.5	44
450	15	yes	0.00	0	10.3
450	15	yes	0.00	0	7.2
400	15	no	N/A	N/A	9.7

^a Polymerization temperature was $105 \pm 1^\circ\text{C}$, and productivity was about 2000 g/g cat.

Table III summarizes experiments done with these catalysts. Some of the catalysts were analyzed for oxidized chromium by iodometric titration. The amount of oxidized chromium was calculated as hexavalent chromium.

B. Activation of Catalysts with Different Gas Flow Rates

Two catalysts were prepared from Davison grade 952 silica, ammonium chromate, and pinacol. A water solution of pinacol and ammonium chromate (pinacol/Cr ratio 4) was combined with the silica to give a slurry (3.3 mL solution/g SiO₂). The slurry was contained in a rotating blender, and the water was removed by heating to 120° and withdrawing the vapor with a vacuum pump. When the evaporation process had removed enough water to leave a free-flowing powder, the catalyst material was transferred to a fiber drum. A 550-g quantity of the ammonium chromate, pinacol, and silica combination was passed through a 40-mesh screen and into a 3-L flask. The material was heated at 150–180°C for 3½ h, and a slow N₂ purge was kept on the flask. A 145-mL volume of titanium tetraisopropoxide was added by drops over 65 min, and heating was continued for 20 min more. The chromium content of the ammonium chromate, pinacol, and silica combination was found by analysis to be 0.65 wt %. The amount of titanium added was 4.2 wt % (Ti/Cr ratio 7).

Catalyst A was prepared from this mixture following the two-step activation previously described (activating 700°C, N₂ + 7% CO, air at 500°C), except that the flow rate of the gases was 600 mL/min.

Catalyst B was prepared with the gas flow at 130 mL/min. Each catalyst was tested in ethylene polymerization and also titrated for oxidized chromium. Results are shown in Table IV.

The effect of a gas flow rate change was also examined for catalysts made with CrO₃. Catalysts C and D were prepared and activated as described in part A, except that the activation gas flow was 600 mL/min in one case and 100 mL/min in the other, and the titanium level was slightly different. Results from these catalysts are also shown in Table IV.

TABLE IV
Activation Variations with N₂/CO Ratio at 700° and Air Treatment at 500°C

Catalyst	Type	wt %	Ti/Cr	Gas flow, mL/min	Cr ⁶⁺ / total Cr	Polym. temp., °C	Yield of cat., g	Melt index
A	AC/P	0.65	7	600	0.22	107	1970	49
B	AC/P	0.65	7	130	0.15	107	2220	23.5
C	CrO ₃	1.0	3.8	600	NA	105	1560	36.5
C	CrO ₃	1.0	3.8	600	NA	105	1736	31.7
D	CrO ₃	1.0	3.8	100	NA	105	1982	10.4
E	CrO ₃ double activated	1.0	3.8	300	NA	105	2009	3.0
F	CrO ₃ control	1.0	3.8	300	NA	105	1974	24.6
G	CrO ₃ TES-TPT	1.0	3.8	300	NA	105	2015	6.5

C. Catalyst Activated First in Air

An 8.0-g quantity of 2% CrO₃-Davison 952 silica was dried in a quartz tube for 1 h at 170°C with N₂ flow at 300 mL/min. A 1.75-mL volume of titanium tetraisopropoxide corresponding to 3.5% Ti was added by syringe to the fluidized bed. After the reaction of the titanium ester, the N₂ was replaced with air at 300 mL/min and the temperature was increased linearly over several hours to 800°C. This temperature was held for 5 h. The temperature was decreased to 100°C, and then the catalyst was given the optimum two-step N₂/CO, then air activation described in part A to provide catalyst E. With a sample from the same lot of silica, control catalyst F was prepared. It was dried, treated with the titanium ester, and activated just like catalyst E, except the heating in air prior to N₂/CO was eliminated. Results for these two catalysts are given in Table IV.

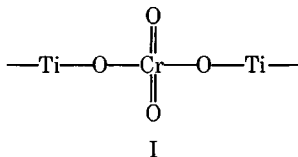
D. Catalyst Treated with Tetraethoxysilane and Titanium Tetraisopropoxide

An 8.0-g quantity of the 2 wt % CrO₃-silica mixture was dried under N₂ fluidization at 300 mL/min at 170°C for 1 h. Tetraethoxysilane (TES), 1.2 mL, was added by syringe and long needle to the fluidized bed so that the TES/CrO₃ molar ratio was 3.5. The yellow color of the catalyst material faded to almost white after about 1 min. Then, 1.75 mL titanium tetraisopropoxide was added to the catalyst bed. The activation was in N₂/CO, followed by air treatment at 700 and 500°C, respectively, with the gas flow at 300 mL/min. This gave catalyst G (see Table IV).

DISCUSSION

The melt index of polyethylene resins is usually a larger number for a sample having smaller average molecular weight and a smaller number for a higher-molecular-weight material. A simple interpretation of the melt index effect caused by the titanated catalysts given the two-step activation is that the active centers have been altered to yield lower-molecular-weight polymers.

Previously,¹¹ we have given evidence to show that titanyl chromate structures (I) are formed in chromium catalysts thermally activated in air:



ESCA indicated an increased electron density on the chromium atoms in such structures relative to silyl chromate structures. The lower molecular weight of polyethylene made with the chromium-titanium catalysts was explained by the weakening of the chromium atom to growing polymer molecule bond, making propagation via monomer insertion and transfer via β -hydride migration more rapid.

The precursor of structure I was shown to contain trivalent chromium. Heating the chromium (III) titanate on silica to 700°F in the reducing mixture of N₂ and CO keeps the chromium in a valence state that is low. Subsequent treatment with air causes part of the chromium to be oxidized (Table III). The extent of oxidation is related to the magnitude of the melt index increase, but the presence of oxidized chromium is not necessary for a noticeable increase in melt index.

Figure 1 shows that the air treatment temperature still affects melt index even when the oxidized chromium is removed by a final treatment with pure carbon monoxide at 400°C. In fact, air treatment at 450°C gave, in one case, a melt index of 10.3, while air treatment at 700°C gave a melt index of only 0.29, even though each catalyst had no detectable oxidized chromium by iodometric titration.

The extent of oxidation can be affected not only by the air treatment tem-

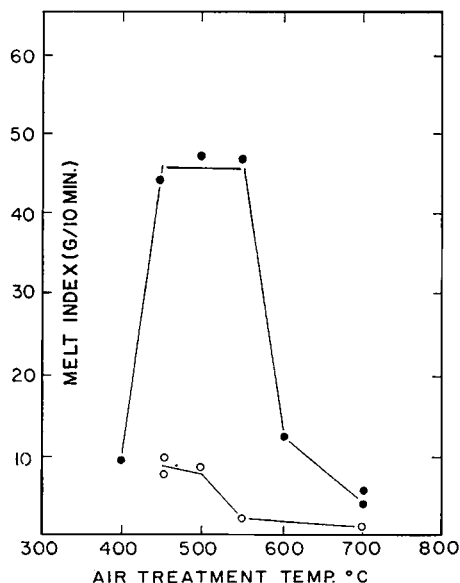


Fig. 1. Effect of air treatment temperature on melt index: (●) catalysts activated in N₂/CO at 700°C for 5 h and treated with dry air for 15 min; (○) catalysts activated and air treated in the same way, but reduced with CO at 400°C after the air treatment.

perature but also by the gas flow rate during the activation. This is shown by the results for catalysts A and B in Table IV. For these two catalysts, the amount activated contained 0.97 mmol chromium compound. At the gas flow rates of 600 and 130 mL/min, the total oxygen passing through the catalyst in 15 min of air treatment is about 73.6 and 15.9 mmol, respectively. In each case, the catalyst is exposed to oxygen in large excess of the stoichiometric amount needed to oxidize all of the chromium. A similar relation of melt index to gas flow rate is shown by catalysts C and D in Table IV.

In any case, partial oxidation would be expected to yield some titanyl chromate structures (I). A close arrangement of titanium and chromium in the activated catalysts is a necessary feature of the high-melt-index catalysts. This fact is demonstrated by the absence of an observable melt index increase when the titanium compound is not added to the catalyst. It is further shown by the result obtained with catalyst G (Table IV). In making this catalyst, tetraethoxysilane was added to the beginning silica-CrO₃ mixture before the titanium ester was added. The silicon ester addition resulted in a color change and thus a reaction of the hexavalent chromium. This reaction of the chromium prevented its subsequent complete reaction with the titanium ester. As a result, the chromium titanate precursor of structure I could not form in high concentration, and consequently only a relatively small melt index (MI) increase was observed, namely, a melt index of 6.5. A control catalyst, not treated with tetraethoxysilane but tested under the same conditions of polymerization, gave an MI of 24.6.

The experiments also show that catalysts which have most of their chromium in the form of titanyl chromate (I) do not give the extremely high melt index values. For example, in Table III, the two catalysts which were treated with air at 700°C had more than half of their chromium in the hexavalent state but gave comparatively low melt index values similar to those obtained by simple air activation. Thus, extensive oxidation of chromium titanate on silica, in contrast with partial oxidation, gives active centers for which the rate of propagation divided by the rate of transfer is higher.

But a limited partial oxidation of chromium titanate on silica is also not sufficient to assure a high-melt-index catalyst. Some subtle feature affected by the thermal history of the catalyst is also involved. Catalyst E was heated to 800°C in air before being given the optimum two-step activation in CO/N₂ at 700°C and 15 min of air at 500°C. The melt index increase was almost totally erased. Other types of high-melt-index thermally activated catalysts are known¹⁴⁻¹⁶ which, by comparison with this experiment, show that it is the thermal and chemical history of the chromium on the silica rather than the titanium on the silica that is the decisive factor. A combination of silica and titanium ester can be heated at 800°C in air to yield a high-melt-index catalyst, provided the chromium is added in an anhydrous manner after such heating.¹⁴ The combination is then further heat treated in air, with air temperatures less than 550°C giving higher-melt-index numbers.

The identity of the catalyst feature that is altered by prior chemical and thermal treatments of the chromium-silica combination is not known. One possibility is the local surface concentration of the chromium. A trivalent chromium ion near a propagating chromium site could influence its electron

density to change the relative rates of propagation and transfer. Crowded propagating sites, on the other hand, could decrease the local concentration of monomer, resulting in a lower molecular weight. Further experiments are planned to identify this feature that is superimposed on the titanium electron density effect. The two effects acting together give a remarkable melt index increase within the temperature limits of the commercial particle-form polyethylene process.

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