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PROCESS FOR THE PRODUCTION OF SHAPED PARTS OF PLASTICIZED POLYETHYLENE

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It has already been suggested to produce shaped parts of polyethylene by compressing finely divided polyethylene, especially polyethylene powder, having molecular weights above 500,000, e.g. above 1,000,000 in several pressure stages; the compressions in the second pressure stage and, if necessary or desired, in the succeeding pressure stages is carried out with simultaneous heating until the material is plasticized.

Thus, blanks, having larger dimensions than those of the finished parts are first produced by mechanical pressure and preferably at room temperature. These blanks are subsequently converted into sintered and plasticized polyethylene by the simultaneous use of heat and of mechanical pressure.

Good results have been obtained by this working method with regard to the quality of the shaped parts produced. Also, the process could be carried out in a simple manner with the devices known in the art. The production of larger shaped parts, however, was limited by the fact that the cold-pressing operation first required very high pressures on the whole surface of the blanks to be finished. The cold-pressing operation requires substantially higher pressures than the succeeding pressure stages effected with the material heated prior to or during the compression.

It has been found that these difficulties can be avoided if the process for the production of shaped parts of plasticized polyethylene mixed, if desired, with other polymers, is carried out in at least two compression stages. In the first of these stages shape-retaining blanks of finely divided material are produced with no increase in temperature which are subsequently plasticized in a second compression stage after having been heated or while being heated; this is done in such a manner that two or more blanks resulting from the first pressure stage are placed together in face-to-face position in the second pressure stage, so that they form an integral shaped part or body after having undergone the treatment effected in the second pressure stage.

It has surprisingly been found in this process that the seams between the individual cold-pressed blanks are frequently no longer visible in the space after sintering. Above all, these seams have the same properties with regard to strength as those of the surrounding portions. The important advantage of the process of the invention resides in the fact that it becomes possible to produce substantially larger shaped parts with the same hydraulic press available.

Thus, for example, slabs of 20 x 20 centimeters and 3 cm. thickness may first to be produced by cold-pressing. These slabs may be placed side by side into a die of 1 x 2 meters. If at least one additional compression is now applied while heating, one single sheet of 1 x 2 meters and 3 cm. thickness is obtained. Seams are no longer recognizable in the finished sheet. According to another embodiment of the process of the invention, heating of the individual slab is not effected in the second compression stage but previously as, for example, is an oven under a protective gas atmosphere.

It is also possible by the process of the invention, for example, to stack 5 slabs each of 10 cm. thickness and press them into a block of about 50 cm. thickness. The production of such a block from a single piece would require excessively long heating periods due to the poor heat conductivity of polyethylene so that the production would become uneconomical. Thus, the process of the invention permits the production of blocks of any thickness desired.

In practice, best results are obtained when the pressure applied in the first stage of the process is at least 5 times that of the pressure used in the second stage. According to a specific embodiment of the process, the blanks obtained from the first stage consist of prisms having 6 surfaces positioned at right angles with respect to one another, or of disks of circular or other form with parallel surfaces. The prisms may be arranged side by side in one layer, or the prisms or disks may be placed one upon another. It is advantageous in many cases to place prisms side by side and in layers.

While in general blanks having the same chemical composition and the same physical properties will be used for the second and, as the case may be, the succeeding compression stages, the process becomes particularly useful by the fact that blanks having different properties can be combined to form an integral shaped part; in that case, it is preferable to operate so that the different blanks are arranged in regular order as, for example, in layers.

Thus, it is possible to combine into one piece cold-pressed pieces of different qualities, e.g. of different colors, different molecular weights, etc., thereby producing laminates having particular color effects and particular properties with regard to strength.

It is favorable in special cases to incorporate other polymers into the polyethylene. The process of the invention is also applicable to the production of shaped parts of plasticized polypropylene.

The process of the invention is primarily applicable to high molecular weight polyethylene, i.e., for example, polyethylenes having molecular weights in excess of 100,000 and preferably above 500,000. Polyethylene of this type is known as "high-density" polyethylene and is produced by the polymerization of ethylene at pressures below about 100 kg./sq. cm. and temperatures up to about 100° C. with the use of catalysts consisting of mixtures of organometallic compounds, especially aluminum alkyl compounds, with compounds of metals of the 4th to 6th subgroups of the periodic table, particularly with titanium compounds as, for example, titanium tetrachloride (see "Angewandte Chemie," vol. 67, 541–547 (1955)).

The molecular weights stated above have been determined viscosimetrically.

The process according to the invention will now be more fully explained in a number of examples, but it should be understood that these are given by way of illustration and not of limitation and that many changes in the details can be made without departing from the spirit of the invention.

Example 1

The polymerization of ethylene was effected in a glass vessel of about 5 liters capacity and equipped with an agitator, into which were filled 2 liters of a C_8–C_{10} hydrocarbon fraction obtained by carbon monoxide hydrogenation. This hydrocarbon fraction had been prepared by hydrogenation, effected at 250° C., subsequent refining with sulfuric acid, and intensive drying. After flushing of the reaction vessel with ethylene gas and heating to about 50° C., the catalyst solution was added while agitating and passing ethylene through the vessel. The catalyst solution had been prepared by mixing together 100 cc. of the same C_8–C_{10} fraction, 1.08 grams of diethyl aluminum monochloride and 0.42 gram of titanium tetrachloride, and vigorously shaking the mixture for about 30 minutes. Upon addition to the catalyst solution, the reaction temperature was adjusted to about 75° C. Atmospheric pressure prevailed throughout the reaction as glass equipment cannot be subjected to elevated pressures. After 12 hours of reaction, 472 grams of polyethylene had formed.

The mixture was filtered and the filter residue was treated with 5 times its quantity of 1% aqueous sodium hydroxyide solution in a stirring flask. The mixture was then heated to the boiling point, thereby distilling off the residue of the hydrocarbon fraction together with the water vapor.

The residue from the distillation was finally washed to free it from alkali and was then dried. The polyethylene obtained had a molecular weight of 1,100,000, as determined viscosimetrically.

760 grams of the high molecular weight polyethylene thus prepared and having an average particle size of 100μ was placed into a die of 20 cm. in width and 20 cm. in length. The mass was cold-pressed at a specific pressure of 100 kg./sq. cm. and at room temperature whereby blanks of 20 x 20 x 2.8 cm. were obtained.

20 of these blanks, in rows of five, were placed side by side into a die of 100 x 80 cm. The die was placed into a press equiped with heatable pressing plates and subjected to a specific pressure of 10 kg./sq. cm. for 6 hours at a temperature of 150° C. Upon cooling, a sheet of plasticized polyethylene having a weight of about 1.5 kg. was obtained. This sheet was completely homogeneous. After sintering of the sheet, the strength measured at the seams between the original blanks was the same as that of the adjacent portions.

By another embodiment, sheets of 100 x 80 cm. were produced by heating the blanks obtained by cold-pressing, in the first compression stage to 160° C. in an oven under a protective gas atmosphere; then the heated slabs were placed side by side into the preheated die of 100 x 80 cm. and compressed in a press which was not heated, or only slightly heated. Here again, sheets having the same good properties were obtained.

Example 2

Polyethylene as prepared in Example 1, i.e. having a molecular weight of 1,100,000 as determined viscosimetrically, was used in this example, too. 38 kg. of this material, in a die of 50 cm. in width and 80 cm. in length, were cold-pressed at a specific pressure of 130 kg./sq. cm. This resulted in blanks of 14.2 cm. in thickness.

The cold-pressed blanks were compressed into sheets in a heatable press for about 8 hours and at a temperature of 160° C. The sheets, while hot, were subsequently placed one upon another and compressed for about 20 minutes under a specific pressure of 18 kg./sq. cm. with no additional supply of heat. A block of polyethylene was obtained having a weight of 152 kg. and a size of 50 x 80 x 32 cm.

The block was completely homogeneous and showed no reduction in strength at the seams.

It should be understood that the process can be carried out with equal success when the laminates are subjected in the second compression stage to pressures of 10–25 kg./sq. cm. at temperatures ranging from 150 to 180° C.

What I claim is:

1. A process for the production of shaped, filled-out solid blocks of plasticized high-density polyethylene in a plurality of compression stages wherein in a first compression stage shape-retaining blanks are produced from finely divided high-density polyethylene which subsequently are plasticized in a second compression stage under application of heat, which comprises compressing said finely divided high-density polyethylene substantially at room-temperature at pressures ranging from 100 to 180 kg./cm.^{2} to form said blanks, placing at least two of said blanks in a face-to-face position, and compressing the same into an integral and seamless unit by subjecting them to temperatures of 150–180° C. and to pressures of 10 to 25 kg./cm.^{2}.

2. The process as defined in claim 1, wherein the pressure in said first stage is at least five times that used in said second stage.

3. The process according to claim 1 wherein the blanks obtained in the first stage consist of rectangles having 6 surfaces located at right angles with respect to one another.

4. The process according to claim 1, wherein the blanks obtained in the first stage consist of circular disks with parallel end faces.

5. The process according to claim 1, wherein the shaped blanks of the first compression stage are arranged side by side in one layer, before they are subjected to further compression.

6. The process according to claim 5, wherein the shaped blanks of the first compression stage are arranged in superposed position before they are subjected to further compression.

7. The process according to claim 1, wherein blanks having the same chemical composition and the same physical properties are used.

8. The process according to claim 1, wherein blanks of different molecular weight are combined to produce an integral shaped body.

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