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(54) PROCESS FOR PURIFYING POLYPROPYLENE

(71) We, ATO CHIMIE, a French Body Corporate, of Tour Aquitaine, 92400 Courbevoie, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for purifying polypropylene obtained by polymerizing propylene with Ziegler type catalysts and containing catalyst residues. By means of the process of the invention both isotactic and atactic polypropylene can be obtained in an improved state of purity, especially as regards the lowering of the content of catalytic residues originating from the polymerisation.

A vast amount of literature is in existence regarding the purification of polypropylene produced by polymerisation in the presence of catalysts which are based on organo-aluminium compounds and transition metals. This purification is in fact very important for the quality of the polymer. It is a question of removing at least the major part of the mineral compounds remaining after the polymerisation. These compounds, which are usually those of aluminium, titanium and chlorine, have an unfavourable action on the stability, the resistance to ageing, the colour and the smell of the polymer.

Following the polymerisation of ethylene or propylene by the process which uses the catalyst of the Ziegler type, based on aluminium diethyl chloride and titanium chloride, the polymer generally contains several hundreds of parts per million of each of the elements Al, Ti and Cl. Experience has shown that, for practical requirements, the contents of these impurities have to be reduced, so as not to exceed about 40 to 50 ppm for Al, 30 ppm for Ti and 30 to 40 ppm for Cl. Among the numerous methods of washing the polymer powder which have so far been proposed, the best results seem to have been obtained by a treatment with an alcohol-hydrocarbon mixture containing gaseous hydrochloric acid, as described in French Patent Specification No. 1,488,777. Although the use of HCl can lead to the production of isotactic polypropylene of suitable purity, in which the content of the aforementioned elements is not more than of the order of 10 to 20 ppm, this process does not permit the obtaining, at the same time, of atactic polymer of acceptable purity. When attempting to extract the atactic polypropylene from the washing liquid used in this known process, then, depending on the proportion of gaseous HCl required for the washing, a product is obtained which includes about 10% to 25% by weight of chlorine in the form of chlorides.

All the aforementioned literature of which we are aware is concerned generally with only washing the isotactic polymer, the atactic polymer being usually left in the discarded residues, which results in a not inconsiderable loss of material. This form of polymer has, nevertheless, a number of uses, particularly in the preparation of coatings, adhesive compositions, varnishes, mastics, and the like, and it is therefore still of interest to be able to separate it economically from the isotactic polypropylene, the production of which is the main object of the manufacturing operation. However, for the recovery of the atactic polymer so that it will be industrially viable, this product must not in its crude state contain too many impurities. As indicated above, the prior art yields a crude atactic polymer which is much too impure.

The present invention enables the isotactic and atactic polypropylenes to be separated under conditions such that each of them can be obtained in the state of

purity which is required industrially. Thus, the process of the present invention makes it possible to obtain, starting with the crude product, an isotactic polypropylene containing less than 5 ppm of Cl, less than 25 ppm of Al and less than 20 ppm of Ti. The separated atactic polymer may not contain more than 3% of the total chlorine, which is perfectly acceptable for its subsequent use, as compared with about 10% to 25% of the prior art.

According to the present invention, there is provided a process for purifying polypropylene obtained by polymerizing propylene with a Ziegler type catalyst and containing catalyst residues, which comprises the steps of:

mixing the polypropylene with a liquid comprising a hydrocarbon, an alcohol, a carboxylic acid and a ketone ester or a diketone;

heating the mixture;

separating solid undissolved isotactic polypropylene from the hot liquid;

rinsing the solid with fresh liquid; and

evaporating the liquids to recover atactic polypropylene dissolved therein.

Preferably, the alcohol-hydrocarbon mixture is selected from those which form azeotropes boiling at temperatures below 100°C; the polymer is kept in the boiling solvent mixture under reflux for the time which is sufficient to separate the atactic polypropylene and the residues of the catalyst system. After separation of the insoluble part by filtration of the liquid, this part is washed with the same solvent mixture, the washing liquid being reunited with that from the treatment at boiling point.

From the washing liquid, the atactic polypropylene can be recovered by evaporation of the solvent, possibly after a neutralisation of the catalyst residues.

The solvent employed preferably includes one or more C_6 to C_8 saturated aliphatic hydrocarbons, particularly hexanes, cyclohexane, heptanes, octanes, C_6 to C_8 or C_6 to C_7 paraffin blends, etc. The alcohols which are preferred for use in admixture with these hydrocarbons are C_1 to C_4 alcohols, particularly ethanol, propanols and butanols. The preferred solvent mixtures are those which form azeotropes boiling above 50°C.

As regards the carboxylic acids which are suitable for carrying the invention into effect, these may be selected from those which have already been proposed in the prior art, particularly in French Patent Specification No. 1,425,590, i.e. the formic acetic, propionic, butyric or valeric acids. It may, however, be highly advantageous to employ substituted acids, polyacids and aromatic acids, such as for example monochloracetic, butane-tricarboxylic, benzoic, acetyl-salicylic acids or another acid of this type.

The diketones which, according to the present invention, improve the elimination of the mineral impurities from the polymers, may correspond to the general formula

$$R^1—CO—CHR—CO—R^2$$

in which R^1 and R^2, which may be the same or different, are hydrocarbon groups, mainly alkyl groups, particularly C_1 to C_6 groups, while R may be a hydrogen or a C_1 to C_6 alkyl group. An examples of such ketones is acetyl acetone, $CH_3CO—CH_2—CO—CH_3$.

Also suitable are ketone esters, in which one of the carbonyls of the diketone is replaced by a carboxyl group, that is to say compounds of the formula $R^1—CO—CHR—COOR^2$, in which R^1 and R^2 are as defined above. It is thus possible to use, for example, an alkyl acetoacetate, this latter preferably being a C_1 to C_6 alkyl, particularly ethyl.

The components of the solvent mixture which are used in the present invention are known *per se* for purifying polypropylene; in particular, the mixtures, of alcohols and hydrocarbons are in use at present for this purpose; however, the specific combination in accordance with the invention, which consists in using such a mixture to which a diketone or ketone ester and, at the same time, a carboxylic acid, are added, is entirely novel and has not so far been proposed for the combined separation of catalyst residues and atactic polymer.

Although β-diketones and keto-esters have already been proposed for washing polyolefines, particularly in U.S. Patent Specification No. 3,281,399, where it is proposed to use these compounds concurrently with alkylenes oxides, they have not enabled the chlorine to be eliminated in a satisfactory manner. It is therefore an unexpected result to have obtained, by means of the present invention, an effective elimination of the impurities, including chlorine, by using the novel combination

agents which include diketones or ketone esters in the hydrocarbon-alcohol-carboxylic acid mixtures.

The treatment of the polymer by means of the solution of selected reactants is preferably carried out at the boiling point of the azeotrope formed by the hydrocarbon and the alcohol. However, thanks to the addition of the ketone compound, the time required for this operation can be shortened. For example, the use of the azeotrope mixture consisting of heptane and isopropyl alcohol with 0.5% of acetic acid requires at least one hour at boiling point, while the addition of acetyl acetone, in an amount of 1% to 3%, permits the time for the washing to be shortened to 30 minutes. Furthermore, and it is here that one of the important advantages of the invention becomes apparent, the concurrent use of the organic acid and of the ketone compound leads to an atactic polymer being obtained which is sufficiently low in impurities, as is the isotactic polymer, to meet the purity standards required.

It is to be noted that the process according to the invention provides a decided advantage, as compared with the known process which uses HCl, in that there is no corrosive action on the equipment, such as occurs with the prior art, and any risk of toxicity is avoided.

Although the proportions of the materials being used may vary within fairly wide limits, depending on the degree of impurity in the crude polymer, they are preferably:— 2 to 10 parts by weight of alcohol-hydrocarbon solvent mixture for 1 part of polymer, 1% to 5% diketone and 0.5% to 4% of organic acid, related to the weight of solvent mixture.

The neutralisation of the filtrate separated from the isotactic polypropylene can advantageously be effected by means of alkaline salts of weak acids such as, for example, acetates, propionates, isopropionates, butyrates and isopropylates of sodium or potassium.

In the examples which follows, the separation of the isotactic and atactic polypropylenes has been effected at the same time as their purification, using a crude polymer powder obtained in polymerisation reactions conducted in the conventional manner. The conditions of such a polymerisation are given below, by way of example.

The reactor proper is dried with heat under vacuum and under an inert atmosphere. One litre of heptane, of which the water content is less than 5 ppm, is introduced into the reactor. When the temperature is 65°C, the solution of aluminium alkyl is heptane and the suspension of $TiCl_3$ catalyst are injected into it. After very brief stirring, the vacuum is caused to reach the pressure corresponding to the vapour tension of the heptane, namely, 0.37 bar. These very rapid operations are followed by the introduction of propylene to a pressure of 1.1 bars, followed by the necessary quantity of hydrogen (transfer agent) and finally propylene; the total working pressure is reached in 8 hours.

This pressure is maintained by continuous addition of monomer, throughout the reaction period, the outlet from the reactor being closed. A safety pellet calibrated to 11 kg ensures safety in the event of a sudden rise in pressure.

The polymerisation temperature is 65°C. The catalyst comprises 2 millimoles of $TiCl_3 . 1/3\ AlCl_3$ and 5 millimoles of $(C_2H_5)_2AlCl$. Al/Ti=2.5.

The partial pressure of H_2 is 0.15 bar and that of C_3H_6 is 7.48 bars. The ratio of H_2 pressure to the total pressure is thus 0.0197:1.

Reaction time: 6 hours.

On completion of the reaction, the residual propylene is degasified and is emptied out by means of a nitrogenn pressure.

In order to effect comparable purification operations following a like reaction, the suspension of polypropylene in heptane is discharged with each test into two identical stirred reactors provided with a double jacket and a filter plate of porosity 3. These glass reactors are each provided at their base with an emptying valve. The separation according to the invention was carried out in one of the reactors, while the separation in accordance with the prior art (using anhydrous gaseous HCl) was effected in the other reactor.

In the following Examples 1 and 2, the separation comprised the following successive operations:

(1) agitation of the crude polymer with the alcohol-hydrocarbon mixture containing carboxylic acid and the ketone compound (operation according to the invention) or with the alcohol-hydrocarbon mixture containing anhydrous gaseous HCl (operation according to the prior art);

(2) rinsing on a filter with the same mixture of solvents.

In Example 3, the following successive operations were carried out:

(1) elimination of the solvent from the polymerisation medium, by filtration under partial vacuum;

(2) agitation of the separated crude polymer with the alcohol-hydrocarbon mixture containing carboxylic acid and the ketone compound (operation according to the invention) or with the alcohol-hydrocarbon mixture containing gaseous anhydrous HCl (prior art);

(3) rinsing on a filter with the same mixture of solvents;

(4) bringing the separated solid once again into suspension in the mixture of solvents;

(5) a fresh rinsing on a filter.

EXAMPLE 1

On completing a polymerisation reaction, carried out as described above, the remaining propylene was degasified and the contents of the reactor were divided into two substantially equal parts; to each of the two fractions isopropyl alcohol was added in a suitable quantity for forming, with the heptane of the polymerisation medium, an azeotropic mixture of 47.6% of isopropyl alcohol with 52.4% of normal heptane; for greater convenience, this mixture will be called IPH in the remainder of the description.

The quantity of IPH was 4 parts by weight to 1 part of crude polypropylene.

To the first reaction there were added, according to the invention, 2% of acetyl acetone and 1% of acetic acid, relative to the weight of IPH. Into the second fraction there was introduced, as in the aforementioned prior art, 0.4% by weight of anhydrous gaseous HCl relative to the IPH.

Each of the two fractions was then subjected to heating under reflux, with boiling of the azeotrope at 77°C.

After 30 minutes of this treatment, hot filtration was carried out, followed by rinsing on a filter with 140 g of IPH. Each filtrate was in its turn separated into two substantially equal parts. From the first part, the solvent was evaporated to bring it to a constant weight, while the second part was neutralised with a 20% solution of sodium isopropylate, after which its solvent was evaporated to constant weight, as above. In this way four samples of atactic polypropylene separated from the liquid which had served for the treatment of the crude polypropylene were obtained.

The following are the quantitative conditions of these operations:

	Treatment according to the invention	Treatment according to prior art
Weight of IPH (isopropanol-heptane) mixture	500 g	500 g
acetyl acetone	2%	—
acetic acid	1%	—
HCl	—	0.4%
isotactic polypropylene recovered	108.5 g	126 g
atactic polypropylene separated:		
by direct evaporation	3.64 g	3.85 g
after neutralisation	3.86 g	4.47 g

Analysis of the Separated Polymers:

Isotactic:

	Treatment according to the invention	Treatment according to prior art
Ash	420 ppm	430 ppm
Ti	30 ppm	27 ppm
Al	83 ppm	88 ppm
Cl	10 ppm	30 ppm

Atactic:

	Evaporation	Neutralisation	Evaporation	Neutralisation
Ash	2.33%	8.42%	3.00%	18.40%
Ti	0.60%	0.56%	0.55%	0.51%
Al	0.62%	0.59%	1.02%	0.84%
total Cl	2.89%	2.85%	26.09%	21.05%
Na	—	3.03%	—	15.71%

The results obtained show that the polymers which had been separated by the process of the invention contained much less chlorine ions than those which resulted from the conventional application of the solvent with HCl. The difference was particularly noticeable with the atactic polypropylene: when purified according to the invention, this required much less base for its neutralisation; it thus contained after neutralisation, much less sodium than the product obtained using the prior method.

EXAMPLE 2

The treatment was carried out as in Example 1, but the proportions of adjuvants in the following IPH mixture were changed:

	According to invention	According to prior art
acetyl acetone in the IPH	1%	—
acetic acid in the IPH	0.5%	—
HCl in the IPH	—	0.1% (proportion used at present in industry)
Weight of isotactic polypropylene obtained	180 g	180 g

Analysis thereof,

	According to invention	According to prior art
Ti	17 ppm	18 ppm
Al	22 ppm	60 ppm
Cl	<5 ppm	35 ppm
Weight of separated atactic propylene	14.5 g	17 g

Analysis thereof after neutralisation:

Ti	0.29%	0.26%
Al	0.49%	0.38%
Cl	1.55%	5.38%
Na	1.60%	4.80%

EXAMPLE 3

In the process according to the invention, the content of acetyl acetone in the IPH mixture was increased.

Following a polymerisation carried out as previously described, the remaining propylene was degasified and the contents of the reactor were divided into two substantially equal parts. With each of these, the liquid was separated from the polymer formed and this latter was suspended in an azeotropic mixture of 47.6% of isopropyl alcohol with 52.4% of normal heptane (IPH mixture).

The quantity of IPH was 4 parts by weight to 1 part of crude polypropylene.

To the first of the said fractions there were added, according to the invention, 3% of acetyl acetone and 1% of acetic acid, relatively to the weight of IPH.

Into the second fraction 0.4% of anhydrous gaseous HCl, relative to IPH, was introduced, as in the aforesaid prior art.

Each of the two fractions was then subjected to heating under reflux, with boiling of the azeotrope at 77°C.

After 30 minutes of this treatment, hot filtration and rinsing on a filter with 140 g of IPH were carried out. The polymer remaining on each of the filters was brought into suspension in 520 g of pure IPH, the said suspension being agitated for about 30 minutes at a temperature of about 66°C. This suspension was then filtered and the separated polymer was rinsed on a filter with 140 g of pure IPH. The various liquid effluents, separated from the solid polymer during the treatment of

the same fraction and containing the atactic polymer, were reunited so as to form a resultant filtrate, and thus there were obtained a first filtrate resulting from the treatment according to the invention and a second filtrate resulting from the treatment according to the prior art.

Each of these filtrates was neutralised with a 20% solution of sodium isopropylate, after which its solvent was evaporated to constant weight. In this way, there were obtained two samples of atactic polypropylene separated from the liquid which had served for the treatment of the crude polypropylene.

The analysis of the crude polymer, prior to separation, was as follows:

Ash	1800 ppm
Ti	395 ppm
Al	543 ppm
Cl	2000 ppm

After the separation, the following results were found:

	Invention	Prior Art
Isotactic polypropylene obtained:	115 g	115 g
Analysis thereof:		
Ti	6 ppm	6 ppm
Al	20 ppm	37 ppm
Cl	<5 ppm	35 ppm
Neutralised atactic polypropylene obtained (contained in the different reunited filtrates)	8 g	8.2 g
Analysis thereof:		
Ti	0.58%	0.58%
Al	0.91%	0.88%
Cl	2.84%	26.00%
Na	3.01%	24.00%

It can be seen that the atactic polymer when separated according to the invention contained 9 times less chlorine and 8 times less sodium than the corresponding polymer which had been obtained according to the prior art.

EXAMPLE 4

On completion of a polymerisation, carried out as previously described, the remaining propylene was degasified and the contents of the reactor were treated to separate the liquid from the formed polymer. This latter was then brought into suspension in an azeotropic mixture of 47.6% of isopropyl alcohol with 52.4% of normal heptane (IPH mixture). The quantity of IPH was 4 parts by weight to 1 part of crude polypropylene.

To the suspension as obtained 2% of acetyl acetone and 1% of butane-tricarboxylic acid, relatively to the weight of IPH, were added.

The mixture thus formed was subjected to heating under reflux, with boiling of the azeotrope at 77°C.

After 30 minutes of this treatment, hot filtration was carried out, followed by rinsing on a filter with 140 g of IPH. The polymer remaining on the filter was suspended in 520 g of pure IPH, the suspension being agitated for about 35 minutes at a temperature in the region of 66°C. This suspension was then filtered and the separated polymer was rinsed on a filter with 145 g of pure IPH. The various liquid effluents, separated from the solid polymer during the treatment and containing the atactic polymer, were reunited in order to forma resultant filtrate. The solvent of this filtrate was evaporated to constant weight and the atactic polypropylene which had served for the treatment of the crude polypropylene was obtained.

On completing the treatment, there were collected 348 g of isotactic polypropylene and 21 g of atactic polypropylene.

Analysis of the isotactic and atactic polypropylenes gave the following results:

Isotactic polypropylene:

Ash	59 ppm
Ti	10 ppm
Al	14 ppm
Cl	<5 ppm

Atactic polypropylene:

Ti	0.44%
Al	0.70%
Cl	2.18%

EXAMPLE 5

A procedure similar to that of Example 4 was followed, but the butanetricarboxylic acid was replaced by the same quantity (1% relatively to the weight of IPH) of propionic acid.

On completing the treatment, there were collected 330 g of isotactic polypropylene and 20 g of atactic polypropylene, the analyses of which gave the following results:

Isotactic polypropylene:

Ti	14 ppm
Al	9 ppm
Cl	<5 ppm

Atactic polypropylene:

Ti	0.46%
Al	0.75%
Cl	2.3%

EXAMPLE 6

A procedure similar to that of Example 4 was followed, but the butanetricarboxylic acid and the acetyl acetone were replaced by acetic acid and ethyl acetoacetate, respectively.

The quantities of acetic acid and ethyl acetoacetate, relatively to the weight of IPH, were 1% and 2%, respectively.

On completing the treatment, 322 g of isotactic polypropylene and 22 g of atactic polypropylene were collected.

Analysis of these polymers gave the following results:

Isotactic polypropylene:

Ti	9 ppm
Al	12 ppm
Cl	<5 ppm

Atactic polypropylene:

Ti	0.42%
Al	0.68%
Cl	2.1%

EXAMPLE 7

Polypropylene was prepared by polymerising propylene in the presence of a catalyst system containing 5 millimoles of $(C_2H_5)_2AlCl$ and 2 millimoles of $TiCl_3 . 1/3\ AlCl_3$, in liquid propylene at 65°C and under a pressure of 26.5 bars.

After 2 hours of polymerisation, the monomeric propylene was degasified and the polypropylene was washed under nitrogen with an IPH mixture (47.6% of isopropyl alcohol and 52.4% of normal heptane), which also contained, by weight, 2% of acetyl acetone and 1% of acetic acid. The operation took place at 77°C, i.e. at the boiling point of the IPH mixture.

After 30 minutes of this treatment, hot filtration was carried out and the solid product remaining on the filter, namely the isotactic polypropylene, was rinsed on the filter with 140 g of pure IPH.

The filtrates were mixed together and the solvent of the resulting mixture was then evaporated so as to isolate the atactic polypropylene.

Following the above treatment, 402 g of isotactic polypropylene and 41 g of atactic polypropylene were collected.

Analysis of these polymers gave the following results:

Isotactic:

Ti	6 ppm
Al	10 ppm
Cl	<5 ppm

Atactic:

Ti	0.24%
Al	0.36%
Cl	1.12%

WHAT WE CLAIM IS:—

1. A process for purifying polypropylene obtained by polymerizing propylene with a Ziegler type catalyst and containing catalyst residues, which comprises the steps of:

mixing the polypropylene with a liquid comprising a hydrocarbon, an alcohol, a carboxylic acid and a ketone ester or a diketone;

heating the mixture;

separating solid undissolved isotactic polypropylene from the hot liquid;

rinsing the solid with fresh liquid; and

evaporating the liquids to recover atactic polypropylene dissolved therein.

2. A process according to claim 1, wherein the proportion of diketone or ketone ester in the said liquid is from 1% to 5% by weight.

3. A process according to claim 1 or claim 2, wherein the acid used is an aliphatic carboxylic acid.

4. A process according to claim 3, wherein the said acid is an acetic, formic, propionic, butyric, valeric, chloracetic or butane-tricarboxylic acid.

5. A process according to claim 3 or claim 4, wherein the proportion of the acid in the said liquid is from 0.5% to 4% by weight.

6. A process according to claim 1 or claim 2, wherein the acid is aromatic.

7. A process according to claim 6, wherein the acid is benzoic or acetyl salicylic acid.

8. A process according to any of the preceding claims, wherein the diketone has the formula $R^1—CO—CHR—CO—R^2$ or the ketone ester has the formula $R^1—CO—CHR—COOR^2$, wherein R^1 and R^2, which may be the same or different, are each a hydrocarbon group and R is a hydrogen atom or a C_1 to C_6-alkyl group.

9. A process according to claim 8, wherein the diketone is acetyl acetone.

10. A process according to claim 8, wherein the ketone ester is ethyl acetyl acetate.

11. A process according to any one of the preceding claims, wherein the alcohol is a C_1 to C_4 alcohol.

12. A process according to claim 11, wherein the alcohol is ethanol, *n*-propanol, isopropanol, *n*-butanol, isobutanol, or tert.-butanol, while the hydrocarbon is a C_6 to C_8 aliphatic hydrocarbon.

13. A process according to any one of the preceding claims, wherein the mixture of alcohol with the hydrocarbon forms an azeotropic system.

14. A process according to claim 13, wherein the azeotropic system is one boiling between 50° and 100°C, and the heating of the crude polypropylene with the said liquid is effected at the boiling temperature of this mixture with reflux.

15. A process according to any one of claims 1 to 14, wherein the liquids are neutralised before being subjected to evaporation.

16. A process according to any one of the preceding claims, wherein from 2 to 10 parts by weight of the said liquid are mixed with 1 part of polypropylene, for a time such that the separated isotactic polymer, when separated, contains no more than 5 ppm of chlorine, and wherein the atactic polymer which is obtained includes less than 3% of chlorine.

17. A process as claimed in claim 1, substantially as herein described or given in the Examples.

18. Isotactic polypropylene which has been purified by a process as claimed in any one of the preceding claims, which contains less than 18 ppm of titanium, less than 15 ppm of aluminium and less than 5 ppm of chlorine.

19. Atactic polypropylene which has been purified by a process as claimed in any one of the preceding claims, having an ash content which does not exceed 10% after neutralisation.

20. Atactic polypropylene as claimed in claim 19 having an ash content of less than 5%.

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