

- 1 -

PROCESS FOR PREPARING GRANULES OF PIGMENTS BY MEANS OF
DOUBLE EXTRUSION

The present invention relates to a double-
5 extrusion production process for coating organic and
inorganic pigments preferably with acrylic, aldehyde
and/or ketone resins in order to provide a particle
composition preferably in the form of granules.

As is known, pigments are solids both of an
10 organic and an inorganic nature which are defined as
such when they are used within a fixing system, such as
resins, absorbing a part of the light and reflecting
their complementary part which forms the colour of the
coated surface.

As such, they are solids with a very irregular
15 surface, which differs from pigment to pigment, and
having the property of interfacing with other
substances completely different from each other and
greatly influenced by the physical and chemical
20 conditions of the contact elements.

Consequently, the formation of the colour,
resulting from the mixture of various pigments, is not
uniform among the various preparations, due not only to
the change in environmental conditions, which vary in
25 each case, but also the differences in properties of
the surface of the pigment and the surface tension
properties of the polymers during melting which, even
though not different from batch to batch, may vary
slightly.

The difficulties of integrating pigments in
30 vehicle systems based on widely varying resins are well
known.

- 2 -

This is true both in the case of powder systems, where contact of the pigment occurs with a polymer resin in the melted state inside an extruder, and in the case of liquid systems where interfacing occurs with polymers (resins) in the form of a solution, emulsion or dispersion diluted both with solvents and/or water, which have a flocculating effect on the system.

At present in the formulations of powder paints, insertion of the pigments is performed by means of simple physical mixing of the said pigments with granules of varying form (chips or flakes) of the resins, which form the vehicle with the addition of chemical additives able to improve the contact between pigment and resin so as to integrate the pigment in the resin, during extrusion where melting of the resin contained in the mix and dispersion or milling of the pigment(s) in a liquid/viscous phase occurs.

This process normally uses single-screw extruders (single-screw Bandera type) which have a pigment milling capacity which is not sufficiently powerful and therefore not exactly suitable for extruding organic pigments with a high colorimetric yield and for this reason are mainly used for inorganic or organic pigments, but in products where formation of the colour and the colorimetric yield are not to be regarded as decisive.

Twin-screw extruders with composite screws (Leistritz type) are normally used and known; these, compared to single-screw extruders, provide a better performance in terms of pigment refining and milling capacity and are therefore used whenever pigments which

- 3 -

are difficult to mill are used and where a high colorimetric yield is required.

Both the single-screw and twin-screw extruders use heat supplied to the extrusion chamber in order to
5 favour melting of the polymer and milling of the pigments in the liquid/viscous phase.

Despite this, the use of twin-screw extruders has also proved to have limitations in terms of dispersion capacity in the case where particularly sophisticated
10 and costly organic pigments are used, such as those developed for use in paints with a good resistance to external agents, transparency for use in metallic paints, high colour tone and high saturation, and where it is required to maximize the degree of dispersion and
15 consequently the colorimetric yield; or also inorganic pigments which are particularly difficult to disperse or in both cases simply in order to be able to increase the concentration of the pigment in the extruded preparations, while maintaining good results in terms
20 of dispersion.

In particular, with the methods known in the art, the fineness and the degree of homogeneity of milling which can be achieved with many organic pigments (such as, for example, magenta dimethylquinacridone Red 122
25 pigment, violet-red betaquinacridone Violet 19 pigment, orange diketo'pyrrolo-pyrrole Orange 73 pigment), are not acceptable for application sectors such as, for example, that of high-performance paints.

The pigment particles remain, in fact, too large
30 (i.e. 5-30 microns for magenta dimethylquinacridone Red 122 pigment, 10-30 microns for violet-red betaquinacridone Violet 19 pigment, and 10-25 microns

- 4 -

for orange diketo-pyrrolo-pyrrole Orange 73 pigment) as well as not being dispersed in a sufficiently homogeneous manner, negatively affecting properties such as the colorimetric yield, the brilliance and the tone.

In all these cases, a second extrusion in a hot extruder has not provided a substantial improvement in the degree of dispersion.

The possible use of extruded solid preparations not only in powder paints or as master batches in plastics, but also as solid substitute preparations, by means of solubilization with solvent, of the milling step, which is typical of liquid paints and inks, has accentuated the limitations and needs mentioned above.

Description of the invention

It has therefore been necessary to develop a novel extrusion process for coating organic and/or inorganic pigments with resins, in order to obtain a formulation in the form of granules which allows the negative aspects of the present situation to be overcome.

This technology, which forms the subject of the present invention, is based on:

- a first extrusion of the resin and pigment based mixture without induced heating;
- a second extrusion with induced heating of the mixture from the first extrusion;
- granulation of the mixture thus obtained.

According to one aspect of the invention, the first extrusion is performed in a co-rotating twin-screw extruder which allows a first step to be performed without induced heating, using only the heat developed naturally by the cutting and friction forces

- 5 -

inside the extruder.

The twin-screw extruder preferred for the invention uses screws with a diameter of 27-110 mm, preferably 30-87 mm, and length 25-48 times the diameter, preferably 32-40 times.

The temperature inside the abovementioned extruder may vary from about 0 to about 50°C, preferably from 5 to 35°C; dividing ideally the inside of the extruder into 9 zones of identical length, the temperature is normally set in the first three zones to 5/15°C, preferably 10°C, in the second zones (3 to 6) to 15/25°C, preferably 20°C, and in the third zones (6 to 9) to 25/35°C, preferably 30°C.

The temperature inside the extruder is controlled both by the cooling set in the first zones of the extruder and by evaporation of the water present as a component of the mix; this is performed preferably by means of a breather valve situated towards the end part in the extruder conveying zone. Control of the temperature is important for keeping the mix in a not entirely melted state so that the cutting forces may exert their action more effectively.

The flowrate of the first extrusion is about 5-20 kg/h, preferably 10-15 kg/h.

The semifinished product, in a shapeless but homogeneous solid state of pigment and resin leaving the extruder after the first step, may contain water in large quantities, something which may make use thereof during subsequent extrusion difficult. In this case, it is preferable to add to the mixture surfactants or dispersants (which are preferably non-ionic, such as

- 6 -

epoxidized sorbitan and soy bean oil esters, preferably epoxidized sorbitan ester), in order to favour wetting of the solid phase and provide a homogeneous mix with good extrudibility characteristics.

5 The extrudate from the first extrusion is then transferred for secondary extrusion; this procedure may be performed both in batches and continuously.

10 The second twin-screw extruder has screws with a diameter of 27-110 mm, preferably 30-87 mm, and length 30/60 times the diameter, preferably 48-60 times the diameter.

15 The temperature inside the abovementioned extruder may vary from about 50 to about 130°C, preferably from 80 to 110°C; dividing ideally the inside of the extruder into 9 zones of identical length, the temperature is normally set, by means of the supply of induced heat, in the first three extrusion zones to 70/90°C, preferably 80°C, in the second zones (3 to 6) to 80/100°C, preferably 90°C, and in the third zones (6 to 9) to 90/110°C, preferably 100°C.

20 The flowrate of the first extrusion is 15-35 kg/h, preferably 20-30 kg/h.

 The extrusion process is completed using a die and pelletizer.

25 The remaining water present in the mix is extracted also by means of application of a vacuum, if necessary, through the breather valve of the degassing system.

30 The fineness of milling and homogenization of the dispersed particles is completed obtaining a very narrow distribution of the particle size curve with

- 7 -

particle size values which are small and less than values of 1-2 microns when measured using an optical microscope with x200 magnification.

5 The melted state of the mass output from the second operation will also allow the production of microgranules by means of a die and water-cutting microgranulator mounted on the extruder head.

10 It should be emphasized that, while a single hot pass produces an irregular milling fineness with diffused presence of particles having a size of 5-30 microns, 10-30 microns, 10-25 microns in each case (when measured using an optical microscope with x200 magnification), a dual cold/hot pass not only reduces the size of the particles to less than 1-2 microns, but
15 also results in perfect uniformity thereof (narrow distribution of the particle size curve) and consequently a higher colorimetric yield.

20 In particular, in the case of formulations based on both inorganic and organic pigments, an aqueous solution of the dispersant is prepared (the water is preferably used in quantities ranging between 10 and 20% relative to the total weight of the formulation); the resin is introduced into the mixer (preferably an open receptacle of the high-speed blade type) and it is
25 wetted with a quantity equal to about 50% of said solution; the pigment is introduced while mixing and the remaining amount of aqueous solution is added; the inert filler is added and, after mixing, the product is discharged and transferred to the extruder.

30 The mixture may also contain mineral reinforcing fillers, such as barium sulphate for example.

Mixing, both in the case of organic pigments and

- 8 -

in the case of inorganic pigments, is normally performed at a speed of between 800 and 2200 rpm.

The granular formulation which can be obtained according to the process of the present invention may be used for the production of granular systems based on resin and pigment and known in the art, and in particular those described in the international patent applications PCT/IT2005/000443, PCT/IT2005/000536, PCT/EP2006/000019 and PCT/IT2006/000588, in the name of the same Applicants and incorporated herein by way of reference.

Description of the plant/process

The plant/process consists of:

a high-speed turbomixer with propeller impeller and number of revolutions ranging from 1000 to 3000 per minute, preferably 2000/2500 rpm, which allows homogenization of the components consisting of pigment(s), resin, additives and water.

A cooled co-rotating twin-screw extruder for the first pass (Leistritz type) suitable for obtaining a perfect cold dispersion of the pigments of the mixture from the turbomixer.

The "cold pass" does not supply heat and therefore avoids complete melting of the resin, but ensures, using only the "friction" heat produced by the high cutting forces which are generated, a perfect dispersion of the pigment, nevertheless obtaining a non-granular shapeless physical form.

A heated co-rotating twin-screw extruder (Leistritz type) in which the mixture melting process takes place, with complete outflow of the aqueous phase.

A microgranulator (Gala underwater pelletizing

- 9 -

type) which is mounted on the extruder head is used for microgranulation of the extrudate in the aqueous phase.

Preferably the granules are produced by means of a water jet cutting granulator of the type produced by Gala Industries Inc. and described in international patent application WO/21371, incorporated herein by way of reference.

A sieving/drying system which consists essentially of a fluid-bed vibrating screen, for separation of the aqueous phase and sieving/screening of the granules from possible formations with a particle size not to specification and associated drying by hot-air means.

The microgranules obtained from the extrusion process which depending on the specific weight of the extruded mixture may have a number variable from 80 to 200 granules per gramme are supplemented with any silica fluidizing additive where required to avoid problems of compaction of the microgranules during storage or transportation in temperature conditions which are not properly controlled and conveyed away for packaging.

The examples which follow are intended to be purely illustrative and non-limiting and identify some of the possible mixtures of compounds to be supplied to the extruder in order to produce subsequently the particle compositions of the invention both in granule and in powder form; the water must not obviously be regarded as a component of the final formulation since it is eliminated during the drying stage; the parts are to be regarded by weight.

- 10 -

Example 1**Conventional single-extrusion process**

	Magenta dimethyquinacridone Red 122 pigment:	25
	Barium sulphate:	20
5	Atmer® 116 (ethoxylated sorbitol ester):	5
	Laropal® A 81 (aldehyde resin):	50
	Water:	12
	Extrusion parameters:	
	Zones 1-3: temp. 80°C	
10	Zone 4-6: temp. 90°C	
	Zones 7-9: temp. 100°C	
	Diameter of the screws: 30 mm	
	Length of the screws: 1560 mm	
	Die and pelletizer mounted	
15	Yield: 15 kg/h	
	Result: milling fineness: 5-30 microns	

Example 2**Double-extrusion process**

20	Magenta dimethylquinacridone Red 122 pigment:	25
	Barium sulphate:	20
	Atmer® 116 (ethoxylated sorbitol ester):	5
	Laropal® A 81 (aldehyde resin):	55
	Water:	12
25	Parameters of first extrusion:	
	Zones 1-3: temp. 10°C	
	Zones 4-6: temp. 20°C	
	Zones 7-9: temp. 30°C	
	Diameter of the screws: 30 mm	
30	Length of the screws: 750 mm	
	Die and pelletizer not mounted	

- 11 -

Yield: 25 kg/h

Parameters of second extrusion:

Zones 1-3: temp. 80°C

Zones 4-6: temp. 90°C

5 Zones 7-9: temp. 100°C

Diameter of the screws: 30 mm

Length of the screws: 1560 mm

Die and pelletizer mounted

Yield: 15 kg/h

10 Result: milling fineness: 1-2 microns

Example 3

Conventional single-extrusion process

Violet-red betaquinacridone Violet 19 pigment: 40

15 Barium sulphate: 10

Atmer® 116 (ethoxylated sorbitol ester): 6

Laropal® A 81 (aldehyde resin): 44

Water: 12

Extrusion parameters:

20 Zones 1-3: temp. 80°C

Zones 4-6: temp. 90°C

Zones 7-9: temp. 100°C

Diameter of the screws: 30 mm

Length of the screws: 1560 mm

25 Die and pelletizer mounted

Yield: 15 kg/h

Result: milling fineness: 10-30 microns

Example 4

30 Double-extrusion process

Violet-red betaquinacridone Violet 19 pigment: 40

- 12 -

	Barium sulphate:	10
	Atmer® 116 (ethoxylated sorbitol sorbitol):	6
	Laropal® A 81 (aldehyde resin):	44
	Water:	12
5	Parameters of first extrusion:	
	Zones 1-3: temp. 10°C	
	Zones 4-6: temp. 20°C	
	Zones 7-9: temp. 30°C	
	Diameter of the screws: 30 mm	
10	Length of the screws: 750 mm	
	Die and pelletizer not mounted	
	Yield: 25 kg/h	
	Parameters of second extrusion:	
	Zones 1-3: temp. 80°C	
15	Zones 4-6: temp. 90°C	
	Zones 7-9: temp. 100°C	
	Diameter of the screws: 30 mm ;	
	Length of the screws: 1560 mm	
	Die and pelletizer mounted	
20	Yield: 15 kg/h	
	Result: milling fineness: 1-2 microns	

Example 5Conventional single-extrusion process

25	Orange diketo-pyrrolo-pyrrole Orange 73 pigment:	40
	Barium sulphate:	10
	Atmer® 116 (ethoxylated sorbitol ester):	5
	Laropal® A 81 (aldehyde resin):	45
	Water:	12
30	Extrusion parameters:	
	Zones 1-3: temp. 80°C	

- 13 -

Zones 4-6: temp. 90°C

Zones 7-9: temp. 100°C

Diameter of the screws: 30 mm

Length of the screws: 1560 mm

5 Die and pelletizer mounted

Yield: 15 kg/h

Result: milling fineness: 10-25 microns

Example 6

Double-extrusion process

10 Orange diketo-pyrrolo-pyrrole Orange 73 pigment: 40

Barium sulphate: 10

Atmer® 116 (ethoxylated sorbitol ester): 5

Laropal® A 81 (aldehyde resin): 45

Water: 12

15 Parameters of first extrusion:

Zones 1-3: temp. 10°C

Zones 4-6: temp. 20°C

Zones 7-9: temp. 30°C

Diameter of the screws: 30 mm

20 Length of the screws: 750 mm

Die and pelletizer not mounted

Yield: 25 kg/h

Parameters of second extrusion:

Zones 1-3: temp. 80°C

25 Zones 4-6: temp. 90°C

Zones 7-9: temp. 100°C

Diameter of the screws: 30 mm

Length of the screws: 1560 mm

Die and pelletizer mounted

30 Yield: 15 kg/h

Result: milling fineness: 1-2 microns

- 14 -

CLAIMS

1. Process for the production of a particle composition containing at least one resin and at least one pigment, comprising the following steps:

5 (a) extrusion of a mixture containing said at least one resin and said at least one pigment without induced heating;

(b) subsequent extrusion, with induced heating, of the mixture obtained from the extrusion according to step

10 (a);

(c) granulation of the mixture thus obtained.

2. Process according to Claim 1, characterized in that step (a) and/or step (b) are performed in a co-rotating twin-screw extruder.

15 3. Process according to Claim 2, characterized in that the screws of the extruder according to step (a) have a diameter of 27-110 mm, preferably 30-87 mm.

20 4. Process according to Claim 3, characterized in that said screws have a length 25-48 times the diameter, preferably 32-40 times said diameter.

5. Process according to Claim 1, characterized in that the temperature inside the extruder according to step (a) varies from about 0 to about 50°C.

25 6. Process according to Claim 1, characterized in that the temperature inside the extruder according to step (a) varies from about 5 to about 35°C.

7. Process according to Claim 1, characterized in that the flowrate of the extrusion according to step (a) is 5-20 kg/h, preferably 10-15 kg/h.

30 8. Process according to Claim 2, characterized in that the screws of the extruder according to step

- 15 -

(b) have a diameter of 27-110 mm, preferably 30-87 mm.

9. Process according to Claim 8, characterized in that said screws have a length 30/60 times the diameter, preferably 48-60 times the diameter.

5 10. Process according to Claim 1, characterized in that the temperature inside the extruder according to step (b) varies from about 50 to about 130°C.

10 11. Process according to Claim 1, characterized in that the temperature inside the extruder according to step (b) varies from 80 to 110°C.

12. Process according to Claim 1, characterized in that the flowrate of the extrusion according to step (b) is 15-35 kg/h, preferably 20-30 kg/h.

15 13. Process according to Claim 1, characterized in that granulation is performed by means of cutting with a water jet.

14. Process according to Claim 1, characterized in that said at least one pigment is organic and/or inorganic.

20 15. Process according to Claim 1, characterized in that said at least one resin is an aldehyde, ketone and/or acrylic resin.

25 16. Process according to Claim 1, characterized in that said mixture contains at least one mineral reinforcing filler.

17. Composition according to Claim 16, characterized in that said mineral filler is barium sulphate.

30 18. Process according to Claim 1, characterized in that said mixture contains at least one dispersant, which is preferably non-ionic.

- 16 -

19. Composition according to Claim 18, characterized in that said dispersant is selected from among sorbitan and epoxidized soybean oil esters, preferably epoxidized sorbitan ester.

5 20. Process according to Claim 1, characterized in that said mixture contains water.

21. Particle composition which can be obtained according to the process of Claims 1-20.

10 22. Composition according to Claim 21, characterized in that it has an average particle size less than 2 microns.

23. Composition according to Claim 21, characterized in that it has an average particle size of 1-2 microns.

15 24. Use of the composition according to Claims 21-23 for preparation of powder paints, liquid paints and plastics.