(19) World Intellectual Property Organization International Bureau





(43) International Publication Date 7 December 2000 (07.12.2000)

PCT

(10) International Publication Number WO~00/73752~A1

- (51) International Patent Classification⁷: G01J 3/46, B29C 45/18, 47/10, B01F 15/04
- (21) International Application Number: PCT/EP00/04913
- (22) International Filing Date: 25 May 2000 (25.05.2000)
- (25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

MI99A001163

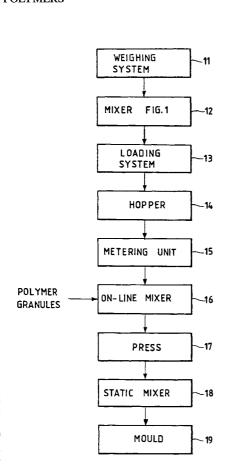
26 May 1999 (26.05.1999)

(71) Applicant (for all designated States except US): EFFECI ENGINEERING S.A.S. DI FOCHESATO ANTONIO & C. [IT/IT]; Via R. Rompato, 19, I-36015 Schio-Vicenza (IT).

- (72) Inventor; and
- (75) Inventor/Applicant (for US only): FOCHESATO COLOMBANI, Filippo [IT/IT]; Via R. Rompato, 19, I-36015 Schio-Vicenza (IT).
- (74) Agents: DE GREGORI, Antonella et al.; Ing. Barzanò & Zanardo Milano S.p.A., Via Borgonuovo, 10, I-20121 Milan (IT).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian

[Continued on next page]

(54) Title: PROCEDURE FOR COLOURING AND/OR COMPOUNDING THERMOPLASTIC AND/OR THERMOSETTING POLYMERS



(57) Abstract: A process for colouring and/or compounding thermoplastic and/or thermosetting polymers directly during the injection-moulding stage or the blow-moulding stage is described. The said process involves the following stages: a first colour-matching stage at which the intrinsic colour of the polymer to be coloured and/or compounded is measured and compared with a specimen of the colour to be obtained in order to identify the exact qualitative and quantitative composition of the colorants needed to obtain the desired colour; the colorants identified and/or the additives are weighed and then mixed; the mixture thus obtained is loaded into a suitable metering unit where it is precisely metered in a predetermined, measured amount and conveyed to the flow of thermoplastic and/or thermosetting granules to be coloured and/or compounded; the material thus mixed is then injection-moulded or blow-moulded.



patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

With international search report.

 Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

"Procedure for colouring and/or compounding thermoplastic and/or thermosetting polymers"

This invention relates to a process for colouring

and/or compounding thermoplastic and/or
thermosetting polymers, a device for the
implementation of that process and a moulded
article coloured and/or compounded by means of the
said process.

- 10 Some methods of colouring and/or compounding thermoplastic and/or thermosetting polymers in the press, ie. directly at the injection-moulding stage or at the blow-moulding stage, are known in the present state of the art.
- 15 However, in the case of technopolymers such as ABS, PPE, PC, etc., the plastic is basically coloured by adding pure pigments during the extrusion process, ie. prior to the injection-moulding stage or prior to the blow-moulding stage.
- In view of the low mixing capacity of the press and the limited dispersibility of the colorants used, it is impossible to colour this type of polymer at

15

20

the injection-moulding stage or at the blow-moulding stage.

In the case of other polymers, such as PE, PVC, PP and PS, only top-grade polymers, ie. those without their own colour, can be coloured and/or compounded. For this purpose concentrates of colorant are pre-dispersed in the same resin that makes up the polymer to be coloured and/or compounded, and extruded in the desired colour, for example in the form of granules.

These pre-concentrates of colorant, called master batches, are currently available in the form of cylindrical granules of various sizes (ranging between 0.5 and 2 cm), or in some cases in the form of coarsely ground polymers. They are prepared by drawing in a twin-screw extruder.

Master batches have a given matrix resin as their base, and can only be used for polymers composed of or compatible with the same matrix because of the partial or complete immiscibility of polymers having different matrix resins.

As already stated, the master batch consequently only allows exact colouring of a neutral polymer,

ie. one without its own colour, which has the same matrix as the master batch or a matrix compatible with it. It is impossible to use the master batch to colour a polymer which already has its own colour, as the final colour will be different from that of the colorant because of the colour contributed by the polymer.

Moreover, two master batches of different colours cannot be mixed directly in the injection press or in the blow-moulding press to obtain a uniform third colour, because the low mixing capacity of the press would produce great irregularities and defects, giving rise to an end product presenting mottling and streaks.

- It is therefore impossible to use colour matching techniques, ie. techniques which mix two or more colours to obtain a uniform third colour, directly at the injection-moulding stage or at the blow-moulding stage.
- The present state of the art thus only allows some classes of polymers to be coloured in the press, directly during the injection-moulding stage or the blow-moulding stage; colouring takes place with the

15

use of master batches directly in the press, but can only be applied to neutral polymer resins, with no colour of their own, which have the same matrix as the master batch or a compatible matrix, and the master batch must already have all the necessary colorants dispersed in it and be usable alone, not in combination with other colouring master batches. In the case of other types of polymer, the colorant is added during the extrusion stage which precedes injection moulding or blow moulding.

Colouring with master batches is based on general parameters that are widely used in injection moulding; the result is that even when the same master batch is used, very different shades of colour may be obtained under different conditions and with different presses and moulds.

The use of master batches does not allow the polymer to be corrected for colour and compounded at the same time to produce a product with particular physical characteristics; for example, fillers of mineral origin cannot be added to produce a more rigid product. In fact, the addition of filler alters the basic colour of the polymer,

WO 00/73752

15

and if colouring is performed with master batches, the desired end result is not obtained.

In the case of translucent products or those with low opacity such as articles made of transparent or coloured PP, in view of the low dispersibility of the master batches it is necessary to work with master batches with a very low pigment concentration (5-10%), which are much more expensive because they present higher unit extrusion costs for the same amount of colorant.

The preparation of a master batch to the customer's specific colour indication, which requires the design of a specific formula, usually takes the master batch manufacturer 2 to 4 weeks, thus involving long waiting times for the moulder between the design of a plastic article moulded in a new colour and its actual production.

The process and the device in accordance with this invention eliminate the drawbacks of the known technique.

In particular, the purpose of this invention is to offer a process and a device that allow practically any thermoplastic and/or thermosetting polymer to

10

15

PCT/EP00/04913

be coloured and/or compounded directly at the injection-moulding stage or at the blow-moulding stage, a wide variety of colours in all possible shades being produced by mixing a few monochrome colouring products compatible with all plastics.

A further purpose of this invention is to offer a process and a device which allow already coloured, recycled and post-consumption products to be coloured and/or compounded to produce the exact colour required.

These and other purposes are achieved in accordance with this invention.

In particular, this invention relates to a process for colouring and/or compounding thermoplastic and/or thermosetting polymers directly at the injection-moulding stage or at the blow-moulding stage, the said process being characterised in that it includes the following stages:

1) a first colour-matching stage at which the
20 intrinsic colour of the polymer to be coloured
and/or compounded is measured and compared with a
specimen of the colour to be obtained in order to
identify the exact qualitative and quantitative

15

composition of the colorants needed to obtain the desired colour;

- 2) the colorants identified and/or the additives are weighed and then mixed;
- 5 3) the mixture thus obtained is loaded into a suitable metering unit where it is precisely metered in a predetermined, measured amount and conveyed to the flow of thermoplastic and/or thermosetting granules to be coloured and/or compounded;
 - 4) the material thus mixed is then injection-moulded or blow-moulded.

The additives can be added directly in the press, instead of to the mixture of colours, by premixing them with the thermoplastic and/or thermosetting granules to be coloured, or adding them continuously with a dedicated metering unit.

This invention also relates to a device for the implementation of the process in accordance with this invention which comprises a manual or automatic weighing system, a rotary mixer, a manual or automatic loading system and a hopper followed by a metering unit connected to a microprocessor,

the said metering unit possibly being connected to an on-line mixer and positioned on an injection press or blow-moulding press, the said press in turn possibly being connected to an additional static mixer and then to a mould.

In particular, the weighing system, loading system and metering unit can be connected to a computerised control and processing system connected to a spectrophotometer.

10 This invention also relates to a moulded article coloured and/or compounded in accordance with the process forming the subject of this invention.

This invention also relates to the use of colorants in the form of microgranules or microflakes, constituted by a concentrate of colorants and/or additives dispersed in a chemical base, mixed together and/or with additives in a colouring and/or compounding process in injection moulding or blow-moulding.

This invention further relates to the use of colorants in the form of microgranules and microflakes, constituted by a concentrate of colorants and/or additives dispersed in a base

composed of mixtures of esters of fatty acids with a melting point of approx. 80°C, the said concentrate being obtained by mixing in a turbomixer or an extruder with a vibrating head, or obtained by any other mixing method, the said colorants, known by the tradenames LEDisperse® and Holcobatch®, being mixed together and/or with additives in a colouring and/or compounding process in injection moulding or blow-moulding.

10 This invention also relates to the use of colorants in the form of microgranules or microflakes, constituted by a concentrate of colorants and/or additives dispersed in a polymer base, such as master batches, mixed together and/or with additives in a colouring and/or compounding process in injection moulding or blow-moulding.

The on-line mixer should preferably be the rotating-shaft type.

The main advantage of the process in accordance

with the invention is that it can be used to colour

and/or compound numerous thermoplastic and/or

thermosetting polymers, producing a wide variety of

colours in all possible shades by mixing a few

monochrome colorant products compatible with all plastics. Above all, the process in accordance with this invention can be used with coloured, recycled or post-consumption starting products to obtain the exact colour desired.

The process in accordance with this invention also enables numerous thermoplastic and/or thermosetting polymers to be compounded and modified chemically during the injection-moulding stage or during the blow-moulding stage, using pure fillers and additives, not only fillers partly dispersed in a matrix resin; in other words, granules pre-extruded and pre-compounded with additives, also known as master batches, are not used.

15 The characteristics and advantages of the product in accordance with this invention will become clear from the following detailed description, provided by way of example and not of limitation.

In particular, the process in accordance with this invention can be applied to the following thermoplastic polymers: high- and low-density polyethylene (HDPE and LDPE), linear polyethylene (LLDPE), acrylonitrile-butadiene-styrene (ABS),

polypropylene (PP), polymethyl methacrylate (PMMA) and its copolymers, polyethylene terephthalate and its copolymers, polybutylene (PET) and its copolymers, (PBT) terephthalate 5 polycarbonate (PC) and its copolymers, crystal polystyrene (GPPS), high-impact polystyrene (HIPS), styrene acrylonitrile (SAN), styrene-based elastomers and thermoplastic rubbers (SB, SBS, SEBS), ethyl vinyl acetate (EVA), crystal polyvinyl 10 chloride, plasticised polyvinyl chloride, acetal resins (POM) and their copolymers, polyamides (6.6, 6.10, 6.11 and 6.12), polysulphones, polyphenylene ether (PPE), olefinic elastomers (EPR and EPDM), cellulose acetate and TUP (thermoplastic urethane).

This process can also be applied to all possible mixtures of the said thermoplastic polymers, individual mixtures and mixtures made by crimping or with the use of compatibilisers.

The process in accordance with this invention can also be applied to thermosetting polymers such as phenol resins, melamine resins and phenol-melamine resins.

The colouring and/or compounding process in the press in accordance with this invention can also be applied to recycled and post-consumption materials in the form of ground polymers, agglomerates and flakes, even if already coloured, as the existing colour can be corrected to the desired colour.

For example, neutral, green, amber, blue, etc. flakes of used PET bottles can be coloured. Colouring in a wide range of shades has been performed in accordance with the procedure forming 10 the subject of this invention with excellent results in the case of both opaque and transparent end products. The colour of ground white ABS originating from recycling of household appliances in numerous colours, including various shades of 15 grey, has also been corrected. The process in accordance with this invention has also produced very good colouring of polymer mixtures formed by virgin and recycled material, such as granules + ground polymers or granules + agglomerates.

The process in accordance with this invention also allows translucent or low-opacity materials to be coloured and/or compounded (e.g. articles made of

20

WO 00/73752

10

13

PCT/EP00/04913

transparent or coloured PP). In view of the greater dispersibility of the colorants used, their physical form and highly precise metering, products with these characteristics, in which the quality of the end product is better in terms of absence of defects, more uniform colour and replicability of colour, can be obtained directly in the press.

The colorants and/or additives used in the process in accordance with this invention are colorants and/or chemicals or fillers in the form of powders, microgranules, microflakes or flakes.

the form of microgranules in Colorants microflakes known by the tradenames LEDisperse® and Holcobatch® have proved particularly suitable for use in the process in accordance with this 15 invention. The colorant known by the tradename LEDisperse®, manufactured by Clariant, concentrate of colorants and/or additives dispersed in a base consisting of mixtures of esters of fatty acids with a melting point of approx. 20 obtained by mixing in a turbomixer. The colorant known by the tradename Holcobatch®, manufactured by Holland Colour, is a concentrate of colorants

and/or additives dispersed in a base consisting of mixtures of esters of fatty acids with a melting point of approx. 80°C, obtained by mixing in an extruder fitted with a vibrating head, or obtained with various mixing methods. In addition, the colorants and/or additives used in the process in accordance with this invention can be constituted by concentrates of colour and/or additives dispersed in a chemical base.

- 10 These colorants can be used individually or in mixtures in any proportion.
- In particular, at stage 1) of the process in accordance with this invention, namely the colour-matching stage, the intrinsic colour of the polymer to be coloured and/or compounded is measured and the exact qualitative and quantitative composition of the colorants which need to be used to produce the desired colour is identified by comparison with a specimen of the desired colour.
- 20 A spectrophotometer exactly measures the visible spectrum of a specimen of the desired colour, exactly measures the intrinsic colour of the thermoplastic and/or thermosetting polymer to be

coloured, and converts it to an item of numerical data. This numerical data item is processed by a specific software program to obtain a precise qualitative and quantitative indication of the colorants that need to be used to obtain the desired final colour.

This program enables "recipes" to be devised for polymers that are very different in terms of both colour and physical form.

- The colour matching stage also takes account of all variables which depend on the type of press, such as the diameter and profile of the screw, the compression ratio, the diameter, the length/diameter ratio, the form of the injection and the mould, and the process conditions. All these variables are considered by the control system of the colour matching stage so as to produce optimum results on variation of the press, even with very different injection systems.
- In practice the software program, ie. the colour matching control system, identifies the qualitative and quantitative composition of the colorant required to produce a final plastic product with a

WO 00/73752

specific, precise colour, and also takes account of all moulding conditions and the press and raw materials used.

At stage 2), the colorants and/or additives in powder, microgranule or microflake form are weighed and then mixed; weighing can be performed manually or automatically. The exact quantities of the individual constituents, which may be constituted by the different monochrome colorants needed to obtain the final desired colour and/or any additives, are then mixed in a rotary mixer to produce a perfectly homogenous mixture; the result is complete, optimum mixing of constituents with a different physical form, chemical nature, apparent density and specific gravity.

The rotary mixer may be of any shape; in particular it could be cubic, rotating around an axis of symmetry passing through two opposite corners.

For example, the rotary mixer shown in figure 1

20 produces complete, optimum mixing of all constituents and also allows easy, fast, thorough cleaning of all inner surfaces.

It can be made of mirror-finish stainless steel 316

L or steel with internal mirror polish and/or chrome-plated, with a length of 70 cm and corners r=5, without welds on the corners and with the welds polished.

The following additives or chemical modifiers can be added directly in the injection-moulding press or in the blow-moulding press when the process in accordance with the invention is used: UV stabilisers, thermostabilisers, crimpers, antistatics, plasticisers, softeners, mineral-based fillers and/or glitters.

As mentioned, the mixture thus obtained is loaded into a suitable metering unit in which it is exactly measured out in a predetermined, measured quantity. The mixture can be loaded manually into the metering unit or automatically into the metering unit positioned exactly on the injection press or on the blow-moulding press.

20 The mixture can be loaded into the metering unit through a hopper.

In particular, the hopper may be made of mirrorfinish stainless steel with polished welds and no

angles exceeding 35°; these characteristics make it particularly suitable for the device in accordance with this invention.

In fact, this solution provides optimum flow of the mixture in the hopper, preventing segregation of the constituents of the mixture. However, the standard hoppers normally used in metering units for presses also give acceptable results.

Although various types of hopper used present the said characteristics, in that the hopper is adapted to the type of press used by the system, two hoppers will preferably be used. The first, shown in figure 2, is made of mirror-finish stainless steel with polished welds; this is the most suitable type of hopper because it presents an inclination of approx 30°, so that mass flow is ensured (there is no stagnation or segregation). It can only be used in association with an automatic (pneumatic) loading system because of its small capacity.

A second type of hopper usable with the process and device in accordance with this invention, shown in figure 3, is also made of mirror-finish stainless

steel with polished welds, and a conical bridgebreaker inside it to prevent the formation of bridges of material, thus improving the internal flow of the mixture.

- 5 The presence of the hopper thus produces optimum flow of the powder, microgranules or microflakes.
 - In particular, the metering unit of the device in accordance with this invention presents a very unusual metering system which allows constant,
- optimum metering of the mixture of colorants and/or additives for any type of flow rate, even very small ones.

This metering unit can be either volumetrically or gravimetrically controlled.

unit of the device in accordance with this invention is self-regulating on the basis of suitable moulding parameters, which can be input into the software control system of the microprocessor to which it is connected. These parameters are weight of moulded item, percentage of colour required, press screw loading time and

material flow index.

PCT/EP00/04913 WO 00/73752

The batcher of the device in accordance with this invention is able to operate with very high precision, even without the weight calibration which is necessary with many other systems. particular, the "flow index" parameter calculated in numerical form when the qualitative and quantitative composition of the colorant and/or additive is identified; this parameter enables the metering unit to regulate itself for exact metering of the composition needed to obtain the desired 10 result, and the long weighing and calibration operation normally required with volumetric-control metering units is therefore eliminated.

5

Thanks to this system, the metering unit of the device in accordance with this invention offers 15 performance and speed of use better than or equal to those of the far more expensive gravimetriccontrol metering units. In fact, a gravimetriccontrol metering unit that can be used in an injection press costs roughly four times as much as 20 a volumetric-control metering unit.

A practical example of the said stages of the process is as follows. If a given number of chairs

need to be coloured a given shade of green, a comparison is made between a specimen of the colour corresponding to the desired colour and the colour of the starting product to be moulded. The system establishes that 99% of thermoplastic and/or thermosetting polymer, 0.2% of yellow and 0.8% of blue needs to be mixed. For a quantity of chairs weighing 5000 kg, the following formula calculated: 4950 kg of polymer, 10 kg of yellow and 40 kg of blue. The mixture of colours (50 kg) is 10 weighed, mixed and placed in a container of suitable size near the press. A pneumatic aspirator extracts the mixture from the container and conveys it to the hopper of the metering unit in such a way that the level of the hopper contents remains 15 constant.

Alternatively, this operation can be performed manually by topping up the hopper at set intervals to prevent it from becoming completely empty.

The metering unit parameters are then entered, with 1% of colour to be metered for 1000 g of moulded product (the chair). The material flow index is also entered, while the loading time is read

22

automatically by a sensor connected to the press. If the loading time is 10 seconds, the metering unit regulates itself to dispense 10 g of colour in 10 seconds, ie. 1 g/s. On the basis of the parameters entered, the metering unit will rotate the metering screw, for example, at 28.5 rpm.

The mixture is therefore continually extracted from the container until it is finished. However, production can be stopped at any time, and the colorant stored for a subsequent process.

10

In practice, the mixture is prepared in batches, in a single operation prior to the moulding process, while the mixture of colours is added to the polymer continuously during the moulding stage.

15 The metering unit preferably used in the process in accordance with this invention is the Movacolor®.

This metering unit is self-regulating on the basis of the moulding parameters, and does not have a metering screw but a cylinder in which the colour advances without being subject to friction or to the pulse input caused by the screw auger. However, any volumetric or gravimetric metering unit could be used.

At stage 3) of the process in accordance with this invention, the mixture is conveyed to the flow of thermoplastic and/or thermosetting granules to be coloured and/or compounded. In particular, the mixture is made to fall in such a way that it intercepts the centre of the flow of thermoplastic and/or thermosetting granules to be coloured and/or compounded to produce a first mixture of raw material/colorant and/or additive. The granules of this first mixture then fall into the press.

If an on-line mixer, such as a rotating-shaft mixer, is installed, the said first mixture falls into the on-line mixer. There, as a result of the thorough mixing performed and higher the temperature in the mixer (due to the flow of hot 15 air which rises by natural convection from the mouth of the press into the mixer), the colorant additive microgranules and/or powders and/or undergo partial softening and stick to the granules of thermoplastic and/or thermosetting material, 20 surrounding and completely covering each individual granule with a layer of colorant and/or additive like a "skin".

WO 00/73752

10

15

20

The material thus mixed falls into the injection press connected to the mould, possibly via a second mixer, and is then moulded.

The said second mixer could be a static mixer such

s as a Sulzer® or Koch® mixer, which further improves
the quality of the colour.

In the case of blow moulding, which is needed to make hollow plastic products such as bottles, containers and the like, the presses used employ a more complex system in which the molten plastic is first moulded or extruded (extrusion blow moulding) to a first form called a preform. Then the preform, in one stage (one-stage process) or in successive stages (two-stage process) is transferred to a special mould where a flow of compressed air allows the preform to expand against the mould walls, thus producing the finished hollow moulding.

Figure 4 schematically represents a possible embodiment of the device for the application of the process in accordance with this invention. It comprises a manual or automatic weighing system 11 connected to a rotary mixer 12, which is connected in turn to a manual or automatic loading system 13

which, via a hopper 14, introduces the homogenous mixture of colorants and/or additives into a metering unit 15 connected to a microprocessor not shown in the figure. The said metering unit 15 is connected to an on-line mixer 16, and positioned on an injection press 17. The flow of granules of the polymer resin to be coloured and/or compounded is conveyed to the said mixer 16.

The lower injection port of press 17 is connected via a static mixer 18 to a mould 19.

The weighing system 11, loading system 13 and metering unit 15 can be connected to a computerised control and processing system which is connected in turn to a spectrophotometer.

With this invention is that it can be used directly at the injection-moulding stage or at the blow-moulding stage for colouring and/or compounding numerous thermoplastic and/or thermosetting polymers, a wide variety of colours in all possible shades being produced by mixing a few monochrome colouring products which are compatible with all plastics. Above all, the process in accordance with

PCT/EP00/04913

this invention can be applied to already coloured, recycled and post-consumption starting products to produce the exact colour required.

A further advantage of the process in accordance with this invention is the speed with which the desired colouring and/or compounding is performed at the injection-moulding stage or at the blowmoulding stage. Any type of starting material can be given the required colour in a time of approx.

15-30 minutes, a result impossible to obtain with 10 any kind of master batch. This means that colours for special resins or customised colours can be prepared in a very short time.

15

20

In addition, the composition of any given shade of colour or the reproduction of any chosen colour can be obtained by mixing a few monochrome colouring products directly in the injection press or in the blow-moulding press. This means that colorants in the form of master batches (predetermined colours for predetermined resins) no longer need to be stocked, thus eliminating numerous expensive colour residues which are of no further use. It sufficient to keep a few (12-15) basic colours of

universal compatibility in stock to colour a huge variety of starting materials in any shade (approx. 95% of the RAL or Pantone chart).

The process in accordance with this invention is

performed with colorants which possess a chemical base compatible with nearly all thermoplastic and/or thermosetting polymers.

10

15

The cost is therefore much less than that of the process using master batches (20 to 70%, depending on the type of polymer resin to be coloured), firstly because the colorant and/or additives used in the process in accordance with this invention have a very high yield, and secondly because the process eliminates the master batch extrusion operation, which considerably increases the final cost of the master batch, especially in the case of customised colours (ie. those made to the customer's specifications) and small batches, where the fixed extrusion costs are very high.

20 The process is also cheaper because it allows a smaller quantity of colorant to be used than in the case of master batches, 1-2% of which is normally used. This quantity of colorant saturates the

28

product to be coloured: in fact, the polymer is already coloured with a quantity of master batch exceeding 0.8%, because the colour of the master batch prevails over the colour of the polymer + master batch system, and the final colour is practically identical to that of the master batch. The further quantity of master batch added serves to increase opacity, ie. to reduce the transparency of the system. As conventional metering units are unable to dispense quantities of master batch under 1% with sufficient precision, causing poor colour distribution, overdosing the master batch and saturating the product with colour is preferred; however, this means a considerable wastage of colour because, as mentioned, the excess colorant 15 only slightly increases opacity. The procedure in accordance with this invention allows the addition of the minimum amount of colorant needed to obtain the desired colour and opacity, without wasting colour to saturate the polymer. The resulting 20 saving amounts to 20 to 50% of the quantity of colorant used.

A great advantage of the process in accordance with this invention is its versatility. It can be applied with excellent colouring and/or compounding results to virgin materials, and especially to heterogeneous materials and recycled and post-consumption materials.

Non-standard thermoplastic materials, which normally only have a yellow or greyish colouring and can only be coloured black with known methods, can be coloured in nearly all shades.

10

15

20

The process in accordance with this invention also enables thermoplastic polymers which are difficult to colour with the use of master batches, such as ABS, PPE, and SBS and SEBS thermoplastic rubbers, to be coloured in the press.

In addition, the process in accordance with this invention allows the polymer to be corrected for colour and compounded at the same time, for example with mineral-based fillers, to obtain greater rigidity or other physical characteristics.

The process in accordance with this invention also eliminates all moulding problems associated with poor dispersal and the preferential flow lines of

30

the molten polymer which are present in the master batch colouring process.

PCT/EP00/04913 WO 00/73752 31

CLAIMS

- Process for colouring and/or compounding 1. thermoplastic and/or thermosetting polymers directly during the injection-moulding stage or the blow-moulding stage, characterised in that it comprises the following stages:
- 1) a first colour-matching stage at which the intrinsic colour of the polymer to be coloured and/or compounded is measured and compared with a specimen of the colour to be obtained in order 10 identify the exact qualitative quantitative composition of the colorants needed to obtain the desired colour;
- 2) the colorants identified and/or the additives are weighed and then mixed; 15
 - 3) the mixture thus obtained is loaded into a suitable metering unit where it is precisely metered in a predetermined, measured amount and conveyed to the flow of thermoplastic and/or thermosetting granules to be coloured and/or compounded;

20

the material thus mixed is then injection-4) moulded or blow-moulded.

- 2. Process as claimed in claim 1, characterised in that the thermoplastic polymer is high- or lowdensity polyethylene (HDPE and LDPE), linear polyethylene (LLDPE), acrylonitrile-butadiene-5 styrene (ABS), polypropylene (PP), polymethyl its copolymers, methacrylate (PMMA) and polyethylene terephthalate (PET) and its copolymers, polybutylene terephthalate (PBT) and its copolymers, polycarbonate (PC) and its copolymers, crystal polystyrene (GPPS), high-impact 10 polystyrene (HIPS), styrene acrylonitrile (SAN), styrene-based elastomers and thermoplastic rubbers (SB, SBS, SEBS), ethyl vinyl acetate (EVA), crystal polyvinyl chloride, plasticised polyvinyl chloride, acetal resins (POM) and their copolymers, 15 polyamides (6.6, 6.10, 6.11 and 6.12), polysulphones, polyphenylene ether (PPE), olefinic elastomers (EPR and EPDM), cellulose acetate, TUP (thermoplastic urethane) and/or mixtures thereof.
- 20 3. Process as claimed in claim 2, characterised in that the mixtures of thermoplastic polymers are individual mixtures and mixtures made by crimping or with the use of compatibilisers.

- 4. Process as claimed in claim 1, characterised in that the thermosetting polymer is a phenol resin, melamine resin or phenol-melamine resin.
- 5. Process as claimed in claim 1, characterised in that the thermoplastic and/or thermosetting polymers are constituted by recycled and post-consumption materials in the form of ground polymers, agglomerates and flakes, even if already coloured.
- 10 6. Process as claimed in claim 1, characterised in that the thermoplastic and/or thermosetting polymers are constituted by neutral, green, amber, blue, etc. flakes of used PET bottles, ground white ABS, or polymer mixtures formed by virgin and recycled material, such as granules + ground polymers or granules + agglomerates.
 - 7. Process as claimed in claim 1, characterised in that the colorants and/or additives are in the form of powders, microgranules, microflakes or flakes.
- 20 8. Process as claimed in claim 1, characterised in that the colorants in the form of microgranules and microflakes are a concentrate of colorants and/or additives dispersed in a chemical base or a base

consisting of mixtures of esters of fatty acids with a melting point of approx. 80°C, obtained by mixing in a turbomixer cr by mixing in an extruder fitted with a vibrating head, or by other mixing methods.

- 9. Process as claimed in claim 7 or 8, characterised in that the colorants can be used individually or mixed in any proportion.
- 10. Process as claimed in claim 1, characterised in that the additives or chemical modifiers are chosen from among the following: UV stabilisers, thermostabilisers, crimpers, antistatics, plasticisers, softeners, mineral-based fillers and/or glitters.
- 15 11. Process as claimed in claim 1, characterised in that the weighing and metering stages are performed manually or automatically.
- 12. Process as claimed in claim 1, characterised in that the mixture is made to fall in such a way that

 20 it intercepts the centre of the flow of thermoplastic and/or thermosetting granules to be coloured and/or compounded and the mixture thus obtained is directly moulded or further mixed, each

individual granule being thus surrounded and covered with a layer of colorant and/or additive that forms a "skin" around it.

- 13. Process as claimed in claim 1, characterised in that the mixture is moulded in a one- or two-stage process involving injection and/or extrusion and/or immersion blow-moulding of preforms.
- 14. Device for the implementation of the process in accordance with claims 1-13 hereof, which comprises

 10 a manual or automatic weighing system (11), a rotary mixer (12), a manual or automatic loading system (13), a hopper (14) followed by a metering unit (15) connected to a microprocessor, the said metering unit (15) possibly being connected to an on-line mixer (16) and positioned on an injection press or on a blow-moulding press (17), the said press in turn possibly being connected to an additional static mixer (18) and then to a mould (19).
- 20 15. Device as claimed in claim 14, characterised in that weighing system (11), loading system (13) and metering unit (15) can be connected to a control

5

20

and processing system which is connected to a spectrophotometer.

- 16. Device as claimed in claim 14, characterised in that metering unit (15) is a gravimetrically or volumetrically controlled metering unit.
 - 17. Device as claimed in claim 14, characterised in that metering unit (15) is volumetrically controlled.
- 18. Device as claimed in claim 14, characterised in

 10 that metering unit (15) has a cylinder instead of
 a metering screw and is self-regulating on the
 basis of the moulding parameters.
- 19. Device as claimed in claim 14, characterised in that rotary mixer (12) has a cubic shape and rotates around an axis of symmetry passing through two opposite corners.
 - 20. Device as claimed in claim 14, characterised in that hopper (14) is made of mirror-finish stainless steel with polished welds and no angles exceeding 35°.
 - 21. Device as claimed in claim 14, characterised in that on-line mixer (16) is the rotating-shaft type.

37

WO 00/73752 PCT/EP00/04913

22. Device as claimed in claim 14, characterised in that the additives or chemical modifiers can be added directly in the injection-moulding press or in the blow-moulding press (17), premixed with the thermoplastic and/or thermosetting granules to be coloured, or added continually with a dedicated metering unit.

5

- 23. Device as claimed in claim 14, characterised in that mixer (18) is a Sulzer® or Koch® static mixer.
- 10 24. Moulded article, coloured and/or compounded in accordance with the process described in claims 1-13 hereof.
- 25. The use of colorants in the form of microgranules or microflakes, constituted by a concentrate of colorants and/or additives dispersed in a chemical base, mixed together and/or with additives in a colouring and/or compounding process in injection moulding or in blow-moulding.
- 26. The use of colorants in the form of 20 microgranules and microflakes, constituted by a concentrate of colorants and/or additives dispersed in a base composed of mixtures of esters of fatty acids with a melting point of approx. 80°C, the

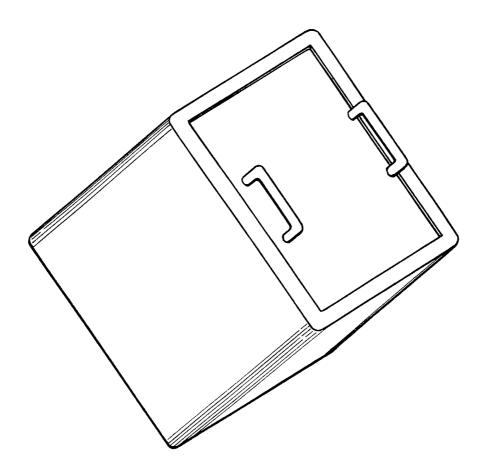
said concentrate being obtained by mixing in a turbomixer or an extruder with a vibrating head, or obtained by any other mixing method, and the said colorants being mixed together and/or with additives in a colouring and/or compounding process in injection moulding or in blow-moulding.

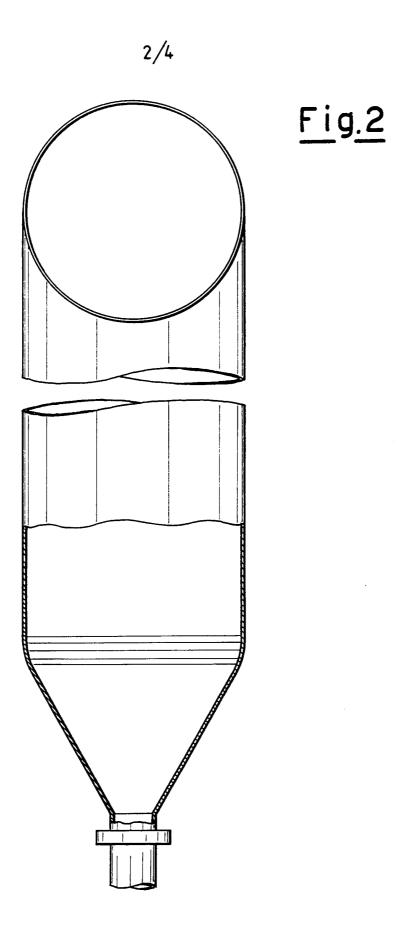
PCT/EP00/04913

27. The use of colorants in the form of microgranules or microflakes, constituted by a concentrate of colorants and/or additives dispersed in a polymer base, such as master batches, mixed together and/or with additives in a colouring and/or compounding process in injection moulding or in blow-moulding.

1/4

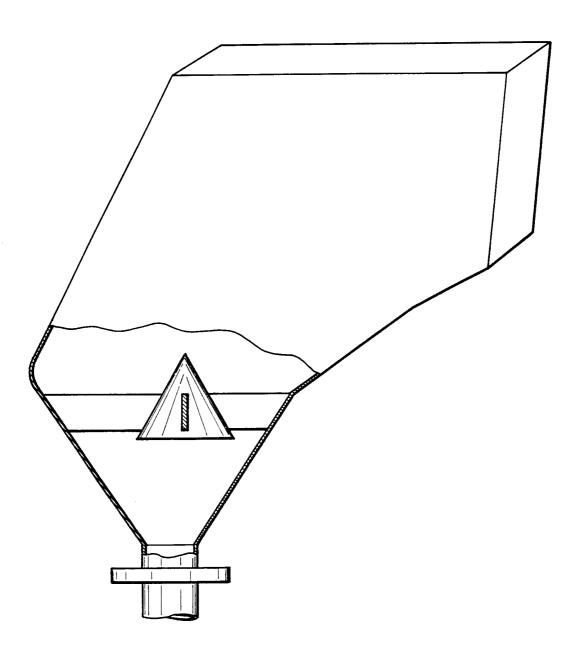
Fig.1



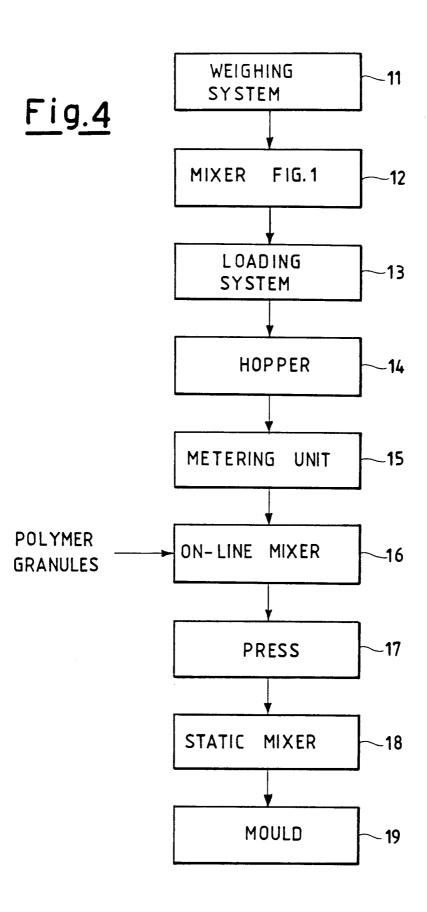


3/4

Fig.3



4/4



INTERNATIONAL SEARCH REPORT

lonal Application No PCT/EP 00/04913

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 G01J3/46 B29C45/18 B01F15/04 B29C47/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

 $\begin{array}{ll} \mbox{Minimum documentation searched} & \mbox{(classification system followed by classification symbols)} \\ \mbox{IPC 7} & \mbox{G01J} & \mbox{B29C} & \mbox{B01F} \end{array}$

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

	Citation of document, with indication, where appropriate, of the relevant passages	
A	EP 0 767 362 A (GEN ELECTRIC) 9 April 1997 (1997-04-09) column 2, line 2 - line 21	1,14,24
A	US 5 568 266 A (CIZA JEAN-CHARLES ET AL) 22 October 1996 (1996-10-22) column 2, line 36 -column 5, line 3	1,14,24
Α	GB 1 119 199 A (PROCESS DEVELOPMENTS LIMITED) 10 July 1968 (1968-07-10) page 1, line 54 -page 2, line 13	1,14,24
A	DE 35 03 361 A (OTTO WILD GMBH & CO KG) 7 August 1986 (1986-08-07) page 4, column 7 -page 5, column 5	1,14,24
	-/	

Further documents are listed in the continuation of box C.	X Patent family members are listed in annex.		
Special categories of cited documents :	"T" later document published after the international filing date or priority date and not in conflict with the application but		
"A" document defining the general state of the art which is not considered to be of particular relevance	cited to understand the principle or theory underlying the invention		
"E" earlier document but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone		
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.		
O document referring to an oral disclosure, use, exhibition or other means			
P document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family		
Date of the actual completion of the international search	Date of mailing of the international search report		
3 October 2000	16/10/2000		
Name and mailing address of the ISA	Authorized officer		
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Herrmann, J		

1

INTERNATIONAL SEARCH REPORT

Intc 'onal Application No PCT/EP 00/04913

	TO DE DEL EVANE	101/21 00/04913
C.(Continua Category °	ation) DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Α	PATENT ABSTRACTS OF JAPAN	1,14,24
	vol. 1995, no. 01, 28 February 1995 (1995-02-28) & JP 06 297509 A (MAZDA MOTOR CORP), 25 October 1994 (1994-10-25) abstract	
A	DATABASE WPI Section Ch, Week 198522 Derwent Publications Ltd., London, GB; Class A32, AN 1985-133217 XP002149120 & SU 1 122 517 A (PLOTNIKOV A I), 7 November 1984 (1984-11-07) abstract	1,14,24
A	PATENT ABSTRACTS OF JAPAN vol. 004, no. 147 (M-036), 16 October 1980 (1980-10-16) & JP 55 101412 A (JAPAN STEEL WORKS LTD:THE), 2 August 1980 (1980-08-02) abstract	1,14,24
X	DE 22 45 022 A (SEVERIN & CO GMBH A) 21 March 1974 (1974-03-21) page 2, paragraph 3; claims 1,3	25–27
A	PATENT ABSTRACTS OF JAPAN vol. 011, no. 050 (M-562), 17 February 1987 (1987-02-17) & JP 61 213121 A (NIPPON ESTER CO LTD), 22 September 1986 (1986-09-22) abstract	25–27
X	EP 0 216 006 A (NEUMUENSTER MASCH APP) 1 April 1987 (1987-04-01) column 2, line 26 - line 36 column 3, line 41 -column 4, line 5	25–27
X	US 5 595 799 A (BECK MARTIN H ET AL) 21 January 1997 (1997-01-21) column 2, line 21 -column 3, line 3; example 1	25–27

1

INTERNATIONAL SEARCH REPORT

information on patent family members

Int tional Application No PCT/EP 00/04913

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0767362	A	09-04-1997	US 5668633 A JP 9202034 A SG 43402 A	16-09-1997 05-08-1997 17-10-1997
US 5568266	Α	22-10-1996	NONE	
GB 1119199	Α		NONE	
DE 3503361	A	07-08-1986	NONE	
JP 06297509	Α	25-10-1994	NONE	
SU 1122517	Α	07-11-1984	NONE	
JP 55101412	Α	02-08-1980	NONE	
DE 2245022	Α	21-03-1974	NONE	
JP 61213121	Α	22-09-1986	NONE	
EP 0216006	A	01-04-1987	DE 3534403 A JP 62073913 A US 4728475 A	02-04-1987 04-04-1987 01-03-1988
US 5595799	Α	21-01-1997	AU 1151897 A WO 9721539 A	03-07-1997 19-06-1997