

COMMONWEALTH OF AUSTRALIA  
PATENTS ACT 1952-1973  
APPLICATION FOR A PATENT

594048

I, We, AUSIMONT S.p.A.

LODGED AT SUB-OFFICE

- 4 APR 1986

Sydney

APPLICATION ACCEPTED AND AMENDMENTS  
ALLOWED 19.12.89.

of 31 Foro Buonaparte,  
Milan,  
ITALY

hereby apply for a grant of a Patent for an invention entitled:

"PROCESS FOR THE PRODUCTION OF COMPOSITE MATERIAL  
BASED ON A POLYMER MATRIX"

which is described in the accompanying complete specification.

This Application is a Convention Application and is based on the  
Application(s) numbered : 20262 A/85

for a Patent or similar protection made in Italy

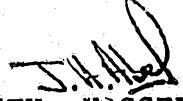
on April 5 1985.

My, Our address for service is care of GRIFFITH HASSEL &  
FRAZER, Patent Attorneys of 71 York Street, Sydney 2000,  
in the State of New South Wales, Commonwealth of Australia.

Dated this 4th day of April 1986.

AUSIMONT S.p.A.

By ~~his~~/their Patent Attorney

  
GRIFFITH HASSEL & FRAZER

To : THE COMMISSIONER OF PATENTS  
COMMONWEALTH OF AUSTRALIA

FORM 8  
COMMONWEALTH OF AUSTRALIA  
PATENTS ACT 1952

DECLARATION IN SUPPORT OF AN APPLICATION FOR A PATENT

In support of an application made by: AUSIMONT S.r.l.  
(formerly AUSIMONT S.p.A.)

for a patent for an invention entitled: "PROCESS FOR THE PRODUCTION  
OF COMPOSITE MATERIAL BASED ON A POLYMER MATRIX"

I, Otilio Masseroli  
of Ausimont S.r.l., 31 Foro Buonaparte, Milan, Italy  
do solemnly and sincerely declare as follows:

1. I am authorized by the above mentioned applicant for the patent to make this declaration on its behalf.
2. The name and address of each actual inventor of the invention is as follows:  
MARIO VISCA of 52, Spalto Marengo, 15100 Alessandria, Italy  
GIANCARLO BOERO of 8/A Strada S. Spirito, 14100 ASTI, Italy  
DARIA LENTI of 45 Via Mazzini, 15048 VALENZA, Alessandria, Italy
3. The basic application as defined by Section 141 of the Act was made as follows:  
in ITALY on April 5, 1985  
in the name of MONTEFLUOS S.p.A.
4. The basic application referred to in the preceding paragraph of this Declaration was the first application made in a Convention Country in respect of the invention the subject of this application.
5. The facts upon which the applicant is entitled to make this application are as follows:  
The inventors made the invention for and on behalf of the basic applicant, MONTEFLUOS S.p.A., in the course of their duties as employees of MONTEFLUOS S.p.A.. MONTEFLUOS S.p.A. was a wholly owned subsidiary of AUSIMONT S.p.A. and the basic application was erroneously filed in the name of MONTEFLUOS S.p.A. rather than in the name of AUSIMONT S.p.A..  
A Deed confirming that the basic application was erroneously filed and that all right, title and interest in and to the invention was the property of AUSIMONT S.p.A. was executed on 9 April 1986 and filed at the Italian Patent Office on 10 June 1986, confirming that at the time of application in Australia, AUSIMONT S.p.A. was entitled to apply pursuant to Section 34(1)(fa) Patents Act 1952. AUSIMONT S.p.A. was subsequently incorporated by merger into AUSIMONT S.r.l. on 30 September 1988.

Declared at Milan, Italy this 8th day of November 1989.

Signed:

AUSIMONT S.r.l.

Position: Managing Director

---

**(12) PATENT ABRIDGMENT      (11) Document No. AU-B-55676/86**  
**(19) AUSTRALIAN PATENT OFFICE      (10) Acceptance No. 594048**

---

(54) Title  
COMPOSITE MATERIAL BASED ON POLYMER MATRIX

International Patent Classification(s)  
(51)<sup>4</sup> C08J 003/16      C08F 283/02      C08F 283/10

(21) Application No. : 55676/86      (22) Application Date : 04.04.86

(30) Priority Data

|             |           |              |
|-------------|-----------|--------------|
| (31) Number | (32) Date | (33) Country |
| 20262/85    | 05.04.85  | IT ITALY     |

(43) Publication Date : 09.10.86

(44) Publication Date of Accepted Application : 01.03.90

(71) Applicant(s)  
AUSIMONT S.P.A.

(72) Inventor(s)  
MARIO VISCA; GIANCARLO BOERO; DARIA LENTI

(74) Attorney or Agent  
GRIFFITH HACK & CO. SYDNEY

(56) Prior Art Documents  
EP 23047

(57) Claim

1. A process for the production of a composite material based on a polymeric matrix comprising, homogeneously dispersed in it, an organic and/or an inorganic filler, said process comprising mixing together the single components in an aqueous phase, and then coagulating the aqueous composite dispersion thus obtained, characterized in that the single components are in the form of aqueous dispersions in which the particles have a surface charge of the same sign and a "Zeta potential" (in absolute value) comprised between 10 and 100 mV, and the ratio (in absolute value) between the "Zeta potentials" of the particles of each dispersion is comprised between 0.2 and 5 and the polymeric matrix is in the form of a latex.

8. A composite material based on a polymeric matrix containing dispersed in it an organic and/or inorganic filler, obtained according to the process as claimed in any one of the preceding claims.

594048

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

Form 10

SUBSTITUTE COMPLETE SPECIFICATION

FOR OFFICE USE

Short Title:

Int. Cl:

Application Number:  
Lodged:

Complete Specification-Lodged:  
Accepted:  
Lapsed:  
Published:

Priority:

Related Art:

This document contains the  
amendments made under  
Section 49.

and is correct for printing.

---

TO BE COMPLETED BY APPLICANT

Name of Applicant: AUSIMONT S.p.A.  
Address of Applicant: 31 Foro Buonaparte, MILAN, ITALY  
Actual Inventor: Mario VISCA ; Giancarlo BOERO and Daria  
LENTI  
Address for Service: GRIFFITH HASSEL & FRAZER  
71 YORK STREET  
SYDNEY NSW 2000  
AUSTRALIA

Complete Specification for the invention entitled:

PROCESS FOR THE PRODUCTION OF COMPOSITE MATERIAL BASED ON  
A POLYMER MATRIX

The following statement is a full description of this  
invention, including the best method of performing it known to  
me/us:-

4834A:rk

The present invention concerns a process for the production of a composite material based on a polymeric matrix. More particularly, the present invention relates to a process for the preparation of a composite material  
5 based on a polymer matrix comprising, homogeneously dispersed in it, an organic and/or organic filler.

As is known, in many applications there are used materials comprising a polymer matrix in which are dispersed organical and/or organic fillers which impart to  
10 the composite material special properties such as colour, a mechanical resistance, etc.

These composite materials in general are produced by mixing the organical and/or inorganic filler in form of a powder to the polymer in form of a powder usually in the presence of a dispersing medium, for example oil. This  
15 type of process requires that the polymer be processable on special machines, and that, moreover, the materials used as fillers possess specific dispersability characteristics.

20 In the case of thermoplastic polymers, there are required both high temperatures as well as a high quantity of energy for the mixing of the filler with the polymer in the molten state.

It is also known to produce composite materials by  
25 using a process consisting in mixing to an aqueous dispersion of the polymer (latex) the filler in form of a powder, and by then coagulating the resulting dispersion and then separating the coagulated composite material. Even if this process of mixing requires small quantities  
30 of energy, the composite material thus obtained does not show a satisfactory homogeneity as required in certain applications.

Moreover, the addition of the organic and/or organic filler, to the latex may lead to the coagulation of the  
35 polymer before a complete homogenization be achieved.

The object of the present invention is that to



provide a process for the preparation of a composite material based on a polymer matrix containing homogeneously dispersed in it an <sup>inorganic</sup> ~~organic~~ and/or <sup>inorganic</sup> ~~inorganic~~ filler, said process not showing the above reported drawbacks.

More particularly, the object of the present invention is to provide a composite material based on a polymer matrix, comprising dispersed an organic and/or inorganic filler, showing a high grade of uniformity, prepared by a quite simple process and with the use of only small quantities of energy.

It has now been surprisingly found that these, and other objects, are achieved only if the following conditions are satisfied:

- a) the polymer matrix and the organic and/or inorganic filler be mixed together in the form of aqueous dispersions;
- b) the particles of the dispersed systems have a high degree of dispersion and show a comparable stability.

According to the present invention, said conditions are satisfied by using the process for the production of a composite material based on a polymer matrix, comprising homogeneously dispersed in it an organic and/or inorganic filler, said process comprising mixing together the single components in the form of aqueous dispersions in which the particles have a surface charge of the same sign and a "Zeta potential" (in absolute value), comprised between 10 mV and 100 mV and the ratio (in absolute value) between the "Zeta potentials" of the particles of each dispersion composed between 0,2 and 5, and then by coagulating the mixing dispersion thus obtained.

"Zeta potentials" (in absolute value) comprised between 15 and 70 mV and ratios (in absolute value) between "Zeta potentials" comprised between 0.5 and 2 are preferred in the process of the present invention.

In the preparation of the composite material, any polymer matrix can be used, provided that it be in the



form of a latex or, preferably, obtained by polymerization in emulsion.

Examples of polymers that may be used in the process of the present invention are: the fluorinated polymers and elastomers such as polytetrafluoroethylene, copolymers of vinylidene fluoride and hexafluoropropylene, the terpolymers comprising vinylidene fluoride; hexafluoropropylene and tetrafluoroethylene terpolymers, or terpolymers vinylidene fluoride, tetrafluoroethylene and perfluoroalkyl-vinyl-ether; copolymers of tetrafluoroethylene and perfluoroalkyl-vinyl-ether, copolymers of tetrafluoroethylene and propylene, copolymers of vinylidene fluoride and chloro-trifluoro-ethylene, copolymers of vinylidene fluoride and hydro-pentafluoropropylene, the terpolymers of vinylidene fluoride, hydro-pentafluoropropylene and tetrafluoroethylene, etc., and the corresponding products comprising in the chain small quantities of trifluoro-bromo-ethylene; the chlorinated (co)polymers such as polyvinylchloride and polyvinylidene-chloride; the polymers and copolymers such as polyacrylonitrile, polymetacrylates, polymethylmetacrylates etc.; polybutadiene, polyisoprene; polycarbonates; acrylonitrile-butadiene-styrene polymers, known as ABS resins; vinyl (co)polymers such as polyvinylacetate, the ethylene-vinylacetate (EVA) copolymers, polyvinyl-alcohol (PVA), etc., and in general any polymer and copolymer obtained with a process of polymerization in emulsion.

Examples of inorganic fillers that may be used in the preparation of the composite material are: pigments, graphite, bronze in powder form, ground glass in the form of spheres or fibres, molybdenum sulphide, silica, steel powder, metal oxides, carbonates, silicates, etc.

As organic fillers can be cited organic pigments, stabilizers, any polymer or resin different from that which forms the polymer matrix, etc.

According to the present invention, composite

materials in which the charge (or filler) is homogeneously dispersed in the matrix, are obtained only if the single components are mixed together starting from preformed dispersions in which the particles are completely wetted by the dispersing medium and show a surface charge of the same sign and comparable stabilities. With the term stability it is meant the capacity of the particles to remain in the dispersed state.

The measure of the stability of a dispersed system may be carried out by the "Zeta potential", defined as the electric potential at the particle-solution plane of slippage. The "Zeta potential" of particles in a dispersion may be determined by means of an electrokinetic measure such as for instance: electrophoresis, electro-osmosis, potential/current flow, etc., as described for example in "Colloid Science", vol. 1, by H.R. Kruyt, published by Elsevier Publishing Co., of 1952.

The adjusting of the "Zeta potential" value of the components of each dispersion may be carried out acting on the mechanisms which control the formation of the surface charge. A suitable method for varying the "Zeta potential" is that of varying the pH of the dispersion or otherwise by adding surfactants, polyelectrolites or ions specifically adsorbed, such as for example: sodium laurylsulphate, ammonium perfluorooctanoate, sodium polyacrylate, sodium hexametaphosphate, sodium phosphate, etc.

After the mixing of the dispersions of the single components, the resulting dispersion is coagulated. The coagulation phase is preferably carried out in a fast way in order to avoid the selective coagulation of the single components of the dispersion, with a consequential dishomogeneity of the coagulate.

Any technique for coagulating the dispersion may be used, such as for instance: vigorous stirring, the addition of electrolites or the addition of a liquid in which the dispersions are not stable or a combination of

said techniques.

The preferred method in the process of the present invention is the addition of electrolites such as sulphuric acid, magnesium nitrate, aluminum sulphate, etc., at a concentration at least sufficient to coagulate the dispersion, combined, if it is necessary, with a vigorous stirring.

The separation of the coagulate from the dispersing medium may be obtained by using conventional techniques such as floatation, filtration, centrifugation, decantation or a combination of said techniques.

The use of the various separation techniques depends on the polymeric matrix used. More particularly, when the polymer phase is polytetrafluoroethylene, a preferred method may be the floatation of the coagulate by using vigorous stirring; while for composite materials based on polyvinylchloride or on tetrafluoroethylene-vinylidene fluoride copolymer, it is advisable to use the separation by filtration.

In order to avoid possible negative influences due to the presence of electrolites in the coagulate, after the separation there may be carried out one or more washings of the coagulate.

The composite material thus obtained according to the process of the invention, under examination at the microscope, is perfectly uniform.

In order to still better understand the present invention the following examples are given, however not to be taken as in any way limitative of the inventive scope of the invention - in the examples all the percentages and the parts are by weight if not indicated otherwise.

#### EXAMPLE 1

A dispersion of a red pigment based on iron oxide (Bayer 110M<sup>®</sup>) was prepared in distilled water, at a concentration of 10 g/l. by means of ultrasounds.

The particles of dispersed pigment showed a "Zeta potential" equal to -25 mV.

Thereupon, 20 ml of the dispersion were added, under a mild stirring (50 r.p.m.) to a polytetrafluoroethylene latex (PTFE) containing 40 g of polymer; the thus obtained dispersion was then diluted with distilled water until  
5 obtaining a concentration of the PTFE equal to 100 g/l. In the latex the PTFE particles showed a "Zeta potential" of -30 mV, measured by micro electrophoresis. To this mixed dispersion thus obtained there were added 10 ml of  $H_2SO_4$  at a 30% by weight, while the stirring speed was  
10 rapidly brought up to 700 r.p.m. The dispersion coagulated completely in a time below 5 min. The stirring was maintained for another 10 minutes in order to float the coagulate.

The powder, separated from the liquid by filtrating  
15 on a nylon net, was then dried for 12 hours at 140°C. A thin ribbon prepared with the pigmented product, showed a perfectly uniform colour, mechanical and dielectrical properties similar to those of a not pigmented ribbon, and the absence of pigment coagulates under microscopic  
20 analysis.

#### EXAMPLE 2

A pigment based on cadmium sulphoselenide (CP 2400, Ferro CO., USA<sup>®</sup>) is dispersed, at a concentration of 10 g/l, of sodium hexametaphosphate, by using a ball mill  
25 of the "Red Devil" type.

The pigment particles have a "Zeta potential" of -46 mV, measured by electroosmosis.

20 ml of the dispersion were then added, under mild stirring (50 r.p.m.), to a PTFE latex containing 40 g of  
30 polymer; the dispersion was thereupon diluted with distilled water to a concentration of 100 g/l. In the latex the PTFE particles showed a "Zeta potential" of -30 mV, measured by electrophoresis. To the mixed dispersion were then rapidly added under constant stirring 20 ml of a  
35  $Mg(NO_3)_2$  1 M solution, thereby causing the bulk coagulation of the particles.

The coagulate was then separated by floating.

increasing the stirring velocity to 700 r.p.m. The powder showed a uniform colouring and was dried at 140°C for 12 hours. A ribbon prepared with the pigmented powder showed a uniform colour, dielectric and mechanical properties similar to those of a non-pigmented ribbon and showed absence of pigment coagulated under microscope analysis.

#### EXAMPLE 3

A sample of graphite (FOLIAC X6236<sup>®</sup>) was dispersed at a concentration of 10 g/l, in an aqueous solution containing 1 g/l of sodium polyacrylate, by using a "Red Devil" ball mill. 60 ml of the dispersion were thereupon added to 120 ml of PTFE latex containing 40 g of polymer.

The "Zeta potential" of the graphite particles, measured by electroosmosis, was -15 mV, while the "Zeta potential" of the PTFE, measured by electrophoresis, amounted to -30 mV. The dispersion thus obtained was then diluted, under mild stirring (50 r.p.m.), up to a volume of 400 ml. Still under mild stirring, there were then added 20 ml of a  $Mg(NO_3)_2$  1 M solution, causing the complete coagulation of the slurry. The thus coagulated polymer was then floated under stirring of about 700 r.p.m.

The obtained powder, dried at 140°C for 12 hours, was perfectly uniform under microscope analysis. A thin ribbon prepared with the dried powder, showed a uniform colour.

#### EXAMPLE 4

40 ml of a slurry obtained by dispersing 25 g of glass fibre in 100 ml of an aqueous solution containing 1 g/l of sodium hexametaphosphate, were added to 120 ml of a PTFE latex containing 40 g of the polymer. The "Zeta potential" of the glass fibre, measured by electroosmosis, was 51 mV, while the "Zeta potential" of the PTFE, measured by electrophoresis, was -30 mV.

The obtained slurry, diluted to a volume of 400 ml, was then additioned with 20 ml of a  $Mg(NO_3)_2$  1 M solution, under a mild stirring (100 r.p.m.). The

addition of the electrolyte caused the complete coagulation of the dispersion. The coagulate was thereupon floated, under vigorous stirring (700 r.p.m.), for a period of 15 minutes. The powder thus obtained, dried for 12 hours at 140°C, at microscope analysis, showed to be formed of glass fibres singularly dispersed in the polymeric matrix.

#### EXAMPLE 5

A PTFE latex was added, in an amount of 10% by weight, to a latex made of Tecnoflon fluoroelastomer (registered Montedison trade mark). The "Zeta potential" of the PTFE latex was -30 mV, while the "Zeta potential" of the fluoroelastomer was -50 mV, both measured by electrophoresis.

Then 200 ml of the mixed latex were slowly added to an equal volume of an aqueous solution containing 8 g/l of  $\text{Al}_2(\text{SO}_4)_3$ , maintained under vigorous stirring (500 r.p.m.). The slurry coagulated instantly.

The coagulate, after separation by filtration and dried for 12 hours at 60°C, appeared under the microscope analysis perfectly uniform.

#### EXAMPLE 6

A PTFE latex, containing 40 g of polymer, was additioned with a dispersion of red pigment CP2400<sup>®</sup> (by Ferro CO., USA) and a  $\text{TiO}_2$  dispersion. The total amount of added pigments was equal to 3.5% on the PTFE. The "Zeta potentials" of the particles are:

- for the PTFE = 30 mV
- for the red pigment = -46 mV
- for the  $\text{TiO}_2$  pigment = -40 mV.

There were prepared various dispersions, with ratios by weight red pigment/ $\text{TiO}_2$  pigment of: 10:1, 2.5:1, 1:1, 1:2.5, 1:5, 1:10 and 1:20.

The dispersions were coagulated as described in ex. 2. The powders, dried for 12 hours at 140°C, were uniformly coloured. The colour of the tablets, obtained by sintering of the powders at 400°C, ranges uniformly

from red to pink as the red pigment/TiO<sub>2</sub> pigment ratio goes down.

EXAMPLE 7

66.7 ml of a polyvinylchloride lates (at a 300 g/l of concentration), 10 ml of dispersion of a yellow F 897 pigment <sup>®</sup> (Ferro Co., USA) (at a concentration 10 g/l) were mixed with an aqueous solution containing 0.1 g/l of sodium hexametaphosphate and 83.4 ml of distilled H<sub>2</sub>O. The "Zeta potentials" of the particles, measured by electrophoresis, were:

for the polyvinyl chloride: -35 mV,

for the pigment : -25 mV.

Thereupon, under a mild stirring, there were admixed 20 ml of a 1 M solution of Mg(NO<sub>3</sub>)<sub>2</sub>, thereby causing the complete coagulation of the slurry.

The coloured coagulate was then separated by filtration and dried for 48 hours at 50°C. The resulting powder was uniformly coloured.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for the production of a composite material based on a polymeric matrix comprising, homogeneously dispersed in it, an <sup>organic</sup> ~~organic~~ and/or an inorganic filler, said process comprising mixing together the single components in an aqueous phase, and then coagulating the aqueous composite dispersion thus obtained, characterized in that the single components are in the form of aqueous dispersions in which the particles have a surface charge of the same sign and a "Zeta potential" (in absolute value) comprised between 10 and 100 mV, and the ratio (in absolute value) between the "Zeta potentials" of the particles of each dispersion is comprised between 0.2 and 5 and the polymeric matrix is in the form of a latex.

2. A process according to claim 1, in which the "Zeta potential" (in absolute value) of the particles of each dispersion is comprised between 15 and 70 mV.

3. A process according to claims 1 or 2, characterized in that the ratio (in absolute value) between the "Zeta potentials" of the particles of each dispersion is comprised between 0.5 and 2.

4. A process according to claim 1 in which the polymeric matrix is obtained by emulsion polymerization.

5. A process according to any one of the preceding claims in which the "Zeta potential" of each component is modified either by varying the pH or by the addition of surfactants, polyelectrolytes or specifically adsorbed ions.

6. A process according to any one of the preceding claims, in which the coagulation phase is performed rapidly so as to avoid selective coagulation of the single components of the dispersion which would result in dishomogeneity of the coagulate.

7. A process according to claim 5, in which the coagulation phase is obtained by the addition of an electrolyte, combined or not with stirring.

8. A composite material based on a polymeric matrix containing dispersed in it an organic and/or inorganic



<sup>filler</sup>  
~~filter~~, obtained according to the process as claimed in  
any one of the preceding claims.

9. A process for the preparation of a composite  
material based on a polymer matrix comprising  
homogeneously dispersed in it an organic and/or inorganic  
filler substantially as herein described with reference to  
any one of Examples 1 to 7.

DATED this 28th day of April, 1989

AUSIMONT S.p.A.

By their Patent Attorneys

GRIFFITH HASSEL & FRAZER

