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(54) **PROCEDE POUR PULVERISER A L'AIR CHAUD DES  
COMPOSITIONS POLYMERES EN POUDRE FONDANT A LA  
CHALEUR**

(54) **METHOD OF HOT AIR SPRAYING THERMALLY MELTABLE  
POWDERED POLYMERIC COMPOSITIONS**

(57) Procédé permettant d'appliquer et/ou de faire fondre par la chaleur, avec éventuellement une thermofixation simultanée ou ultérieure, des polymères en poudre fondant à la chaleur. Selon le procédé, on utilise des générateurs d'air chaud et des convecteurs ayant une vitesse et une température variables (chalumeaux à air chaud pour revêtements ou colles en poudre à pulvériser).

(57) Method of applying and/or heat melting with optional contemporaneous or subsequent thermosetting thermally meltable powdered polymers by using hot air generators and convectors with variable velocity output and temperature. (Heats Guns for spray powder coatings or powder adhesives).



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<p>(21) International Application Number: PCT/EP97/04161</p> <p>(22) International Filing Date: 26 July 1997 (26.07.97)</p> <p>(30) Priority Data: MI96A001728 8 August 1996 (08.08.96) IT</p> <p>(71) Applicant (for all designated States except US): VIANOVA RESINS S.P.A. [IT/IT]; Via Matteo Bianchin, 62, I-36060 Romano d'Ezzelino (IT).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): FARRONATO, Silvestro [IT/IT]; Via Don Sturzo, 43, I-36060 Romano d'Ezzelino (IT). GAZZEA, Sergio [IT/IT]; Via Raffaello Sanzio, 13, I-36060 Romano d'Ezzelino (IT). MARIKAR, Faruq [US/US]; 86 Morris Avenue, Summit, NJ 07901 (US).</p> <p>(74) Agent: RICCARDI, Sergio; Riccardi &amp; Co., Via M. Melloni, 32, I-20129 Milano (IT).</p>	<p>(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, US, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: METHOD OF HOT AIR SPRAYING THERMALLY MELTABLE POWDERED POLYMERIC COMPOSITIONS</p>		
<p>(57) Abstract</p> <p>Method of applying and/or heat melting with optional contemporaneous or subsequent thermosetting thermally meltable powdered polymers by using hot air generators and convectors with variable velocity output and temperature. (Heats Guns for spray powder coatings or powder adhesives).</p>		

"METHOD OF HOT AIR SPRAYING THERMALLY MELTABLE POWDERED  
POLYMERIC COMPOSITIONS"

[Description]

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Powder paints are up to now used almost exclusively in industrial plants as they need cumbersome static equipment such as baking ovens and application booths.

In order to remove these limitations flame guns were recently made available, allowing to apply thermoplastic powder paints in an open atmosphere through an  
10 annular flame which melts the projected powder paint. The molten paint deposits on a support, but the presence of the flame limits its use only to thermoplastic paints of high molecular weight. Moreover, to avoid combustion of the deposited molten paint it is necessary to move continuously and rapidly the point of projection of the flame.

To apply hot melts heat guns are used, comprising glue sticks pressed against a  
15 heated nozzle that melts them, allowing only their spreading. Furthermore hot air dryers are available on the market, that are used for packaging articles with shrinkable films. Up to now, use of hot air generating apparatus to apply *thermosetting* meltable powdered compositions was not known.

*Several portable apparatus mostly in the form of guns comprising usually two  
20 feeding ducts with the possibility of heating, interruption and regulation of the flow, the one for air/paint mix and the second for air, are known. However, none of these guns has optimal features for the specific use with thermosetting powdered compositions: as a matter of fact these compositions must have the possibility of being spread and hardened under controlled adjustable conditions, but this fact is not  
25 guaranteed by prior art solutions.*

*For instance the application of an adhesive based on the mix of a thermoplastic polymer (80%) and a thermosetting polymer (20%) is disclosed in patent US 3 076  
214, but in this case neither the air flow nor the temperature are adjustable and  
because of the excess of thermoplastic polymer in the mix, high and uniform  
30 temperatures are needed.*

*US 3 958 758 also concerns thermoplastics, whose application is carried out by*

*a single body apparatus, that is to say without separating air delivery from material one. This apparatus is able to spray only molten material without the possibility of regulation.*

*Similar apparatus are disclosed in US 4 065 057 and US 5 503 872 but none  
5 of them describes the possibility of dividing air and material feeding flowing out and regulating temperatures and outputs.*

~~*The apparatus described in US 5 338 578 may give good results only if it is used with materials which have been made electrically conductive ( e. g. by means of inclusion of carbon black)*~~

10 *In EP A 0 080 310 concerning the accomplishment of high thickness thermoplastic composites, neither the expansion nor the hardening step of a thermosetting resin can be carried out by using the apparatus.*

As it was realized that the flame, in view of the excessive heat delivered, charred already in the nozzle the powdered paint, *because in the case of thermosetting paint  
15 the viscosity in the molten state and the softening point are remarkably lower than those of thermoplastic polymers*, it was devised that by substituting a hot air flow for the flame, it was probably possible to melt and harden the paint. Therefore with a normal electrostatic gun a powder paint was deposited on some aluminum panels, then a conventional hot air dryer with variable temperature, used for thermally shrinkable  
20 packaging films, was used for projecting hot air on the surface coated with powder paint but said panels were not acceptable because air output was too strong and most paint was blown off.

<Insert page 2a>

Thereafter the air output was reduced by partially covering air intake and it was surprisingly discovered that by regulating the air input it was not only possible to melt  
25 and harden the paint without blowing it out, but it was also possible to expand and spread it in the molten state, just as if it were done with a brush.

Having proven that the principle of using hot air for the flame was a valuable idea, then a gun for projecting powder and a hot air dryer were designed in such a way that the outgoing hot air envelopped the gun nozzle, thus the powder was deposited in  
30 a partially molten condition. Then temperature of the dryer was increased until the projected powder was deposited in a molten condition and thereafter discontinuing

[to be inserted at page 2, after line 22]

A method which uses air instead of the flame is disclosed in US 5 338 578 in which a thermosetting powder coating composition is applied to a substrate by means of conventional powder coating technique. In this case, firstly, the substrate is preheated before the application of the powder composition at a temperature above the melting temperature of the powder composition so that the powder melts upon the contact with the surface of the substrate and then a subsequent heating is carried out in order to complete the curing of the molten powder. As a consequence, there is still the need of a method of applying the powder paint which avoids the paint to be blown out or allows the paint to be applied on sensitive substrates.

delivery of powder it was possible to crosslink it.

Subsequently we tried to apply it in the molten condition on non conductive support and we found that it adhered perfectly on *ceramics, glass*, wood, plastics, paper, fabrics and the like just because it was deposited in the molten condition, and  
5 when applied in such a condition to metal supports it was no longer necessary that the gun was tribochargeable or electrostatic.

In view of the foregoing the method of the present invention consists of the use of at least one equipment comprising at least one gun for spraying the powdered paint or glue and at least one dryer for delivering hot air with variable temperature and  
10 output, possibly with a single nozzle so that the gun and dryer may be used contemporaneously or alternately according to the need. The method allows the application of any meltable powdered composition or thermoplastic or thermosetting polymer on any kind of support or surface.

*These objects are obtained by means of a method as stated in Claim 1, the*  
15 *features of which are stated in the dependent claims.*

~~| Such a method has practically no limitations, as the powdered product to be applied may be projected in powder form from an adjustable close distance and can deposit on a surface in a molten or powdered condition. At the same time or subsequently the polymer can be melted and cross-linked by heat using the dryer part.  
20 Alternatively, the dryer can first be used to preheat the surface on which the powdered polymer is applied with the gun and then is melted during or after said application. |~~

As the equipment has a reduced size, it may be used as a single unit or a set of units, it may be movable or fixed, and it allows to paint either static or large surfaces, or small surfaces even for retouching purposes, by applying the paint melted at a  
25 temperature lower than the cross-linking. With the same technique it is also possible to paint thermally sensitive supports *such as wood or plastics*, or to apply a powdered photohardenable paint, melting it and subjecting the applied film to UV radiation when it is still hot or after cooling. It is also possible to paint with thermosetting powder paints which are caused to melt and expand, controlling that they are perfectly spread  
30 and faultless, and subsequently they can be thermoset at any desired time and with any heat source such as hot air, flame, IR ovens, EB and so forth.

In order to better illustrate the present invention, some non limiting examples of embodiments thereof are given hereinafter. All parts are by weight unless where otherwise specified.

5 Example 1:

By using at the same time the gun and the dryer with delivery of hot air at a speed of about 40 km/h (2,200 foot/min) and at a temperature of 250°C a hybrid polyester-epoxy powder paint comprising:

	Alftalat AN 783	390
10	Epoxide resin (EEW 700-900)	180
	Additol XL 496	30
	Degassing agent	5
	Blanc Fixe	105
	TiO <sub>2</sub>	290

15 was sprayed in a molten condition on a steel sheet having a size of 6 x15 cm coating it uniformly with a layer about 60μ thick, then stopping spraying and at the same time raising the air temperature to about 500°C, only hot air is projected for 2 minutes to obtain cross-linking.

The steel sheet is then subjected to analysis tests by comparing it with a sheet  
20 painted in the traditional way and hardened in an oven at 180°C for 20 minutes and it results in being equal to the standard sample.

In order to highlight the good qualities of the method according to the present invention, namely that hot air can be used to melt and harden a thermosetting powdered paint, the same paint was applied with the gun only on a sheet and then the  
25 dryer was used with a hot air output lowered to 9,1 km/h (500 foot/min), reducing the air inlet opening to avoid that the deposited paint is removed and with the temperature adjusted to 200°C the deposited paint melted and expanded. After fusion, the output was raised to 36,6 km/h (2,000 foot/min), the temperature to 400°C and this condition was held for 3 minutes. Also this steel sheet resulted in hardening like that hardened in  
30 an oven at 180°C for 20 minutes.

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Example 2:

Following the same procedure of Example 1 a polyester-polyurethane powder paint is deposited, consisting of:

	Alftalat AN 745	456
5	Additol XL 432	114
	Additolo XL 496	30
	Degassing agent	5
	TiO <sub>2</sub>	395

10 Example 3:

Following the same procedure of Example 1 a transparent acrylic powder paint is prepared, consisting of:

	Synthacryl LH 897	721
	Additol VXL 1381	216
15	Additol 03551	30
	Degassing agent	3
	UV Stabilizer	30

and it was sprayed in a molten condition on two steel sheets.

Thereafter a sheet is undergoing the analysis tests by comparing it with a sheet  
20 painted in the traditional way and hardened in an oven at 180° C for 20 minutes and it resulted to be equal to the standard sample.

Then from the second painted and hardened sheet a portion of the deposited paint was abraded with a steel brush and with the same procedure the paint was again applied on the abraded portion. After having discontinued the spraying operation, with  
25 hot air kept at the same temperature and increasing the output speed, the paint applied in the molten condition was expanded so that the retouched portion resulted to be uniform. Thereafter the output speed was reduced and air temperature increased to 500° C so as to crosslink the paint in 2 minutes. In this way, even the second, retouched sheet resulted to be equivalent to the standard sample.

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Example 4:

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A transparent UV hardenable powder paint consisting of:

	Alftalat VAN 1743	642
	Additol 03546	275
	Additol VXL 9824	50
5	UV Photoinitiator	30
	Degassing agent	3

was projected in a molten condition on two small wooden boards, coating them with a layer about 100 $\mu$  thick, then one board was subjected with the still molten paint to UV radiation for 30 seconds, while the other board was cooled and after some days  
10 subjected with the applied cold paint to the same radiation but for one minute and surprisingly also the second board, when subjected to the acetone soaked cotton flock test, passed 100 back and forth rubs.

### Claims

1. Method of spray applying powdered thermosetting paints on substrates wherein a hot air generator/convector of known per se with variable temperature, speed and output and with the possibility of separated air and paint delivery by means of one or more nozzles is used, which method comprises the following steps:
- 5 a) delivering a flow of the paint at temperature, output and speed set according to the thermosetting paint to be applied;
- b) interrupting said flow by delivering hot air at temperature and output adapted to promote paint expansion;
- 10 c) hardening the film,
- characterized in that said substrate are sensitive supports and said flow is a hot air/paint mix so as to apply the powder in a molten or partially molten condition.
2. Method according to Claim 1 characterized in that step c) is carried out either by delivering an air flow at higher temperature and lower output than those in step b) or by
- 15 irradiating said film through EB, microwaves, UV and IR irradiation.
3. Method according to any one of Claims 1 and 2 wherein the application step a) takes place through the application of an electrostatic field generated outside or inside the nozzle.
4. Method according to any one of the preceding claims characterized in that the
- 20 regulation of temperatures and outputs of generator/convector apparatus is obtained respectively by adjustable electric resistances or other sources generating heat or by an adjustable air intake conveying the flow with adjustable output and speed onto the support through the heat source.
5. Method according to any preceding claims characterized in that said apparatus known
- 25 per se is portable and in the form of a gun, supplied with a heat generator having variable power, an air convector having variable output and powdered paint projector having adjustable output.
6. Method according to any one of the preceding claims, wherein the powdered thermosetting meltable polymers may be selected from the following groups:
- 30 A) Epoxy or glycidyl compound in combination with di-or polyamines, or dicyandiamide and/or substituted dicyandiamides, or saturated or unsaturated

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carboxylated polyesters, carboxylated acrylics or polyanhydride or polycarboxylic compounds;

B) Hydroxylated compounds such as saturated and unsaturated polyesters, acrylics and the like, in combination with polyanhydrides, or block polyisocyanates or polyurethidiones;

C) Carboxylated compounds such as polyesters or acrylics in combination with hydroxyalkylamides;

D) Unsaturated polyesters and/or acrylated acrylics and the like in combination with photoinitiators and subsequent use of UV lamps or in combination with dialkyl or diacyl peroxides, or peroxyesters or peroxy ketals thermally activated at temperatures higher than the melting point; and

E) Mixtures of groups A, B, C and D.

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