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(54) Title: POWDER COMPOSITIONS BASED ON UNSATURATED POLYMERS FOR THE PRODUCTION OF MAT PAINTS, PROCESS OF PRODUCTION AND APPLICATION THEREOF

(57) Abstract

Powder compositions which are thermomeltable and hardenable by means of radiations or peroxides or catalysts comprise as binder a mixture of two or more paints which are separately or parallely extruded by two extruders, one paint containing an unsaturated amorphous polymer and the other containing a crystalline unsaturated polymer, and/or different from each other for equivalent weight of unsaturation.

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"POWDER COMPOSITIONS BASED ON UNSATURATED POLYMERS FOR THE PRODUCTION OF MAT PAINTS, PROCESS OF PRODUCTION AND APPLICATION THEREOF"

The globalization of the markets which forces the manufacturer to be more competitive and the increasingly higher awareness of respecting and preserving the environment in which we live compel human beings to manufacture by taking into account "three Es" and that is to say Ecology, Energy and Economy. Hence, the producer must not pollute and make products of increasingly higher quality, reducing as much as possible the energy consumption, production time and the overall costs and so being always at the TOP (Total Operational Performance) and in continuous development,

Paints are also in continuous development and the old paints based on solvents and more and more dropping in demand have been replaced firstly by high dry paints, that is to say with less solvent, and then by watersoluble and powder paints, which are continuously on the increase and development.

These latest paints have the good quality of being totally used and without waste because the application excess can be recovered and used again.

First thermoplastic paints have been replaced by thermosettable ones with different types of polymers and several crosslinkable or thermosettable systems and with lower and lower crosslinking time and temperatures.

Powder paints in various crosslinking systems generally give high glossy coatings with good chemical-physical features such as flexibility, hardness and resistance to chemicals and weather agents with gloss being equal to or above 90% when measured under an angle of 20° or 60° according to rule ASTM D 523.

Therefore it has always been a problem to obtain semiglossy or mat coatings with powder paints and thereby several methods which introduce into the different powder paints besides the binder, pigments and traditional additives, one or more opacifier agents such as silica, metal salts, waxes, talc and the like have been suggested. Nevertheless gloss reduction is often insufficient and the chemical-physical features deteriorate and therefore in order to avoid this there are several patents among which for instance the following are cited:

FR 78 04 685 discloses mat films which are obtained by a powder paint consisting of intimate mixture in an extruder of two hydroxyl resins having different hydroxy number along with polyanhydridic hardener.

DE 23 24 696 discloses mat films obtained by a powder paint consisting of intimate homogenization in extruder of a glycidic or epoxydic resin along with anhydridic salts of polycarboxylic acids.

DE 32 32 463 discloses mat films obtained by a powder paint consisting of intimate mixture of a hydroxyl polyester resin along with a blocked isocyanic hardener containing carboxylic acids and a co-crosslinker containing glycidylic groups.

JP 101963 of August 25,1977 (Showa 52) discloses mat films obtained by an eutectic mixture of two paints in epoxydic powder having different reactivity and obtained by the same epoxydic resin but catalized with different amounts of the same catalyst.

In patent application EP 0 551 064 A2 of UCB powder paint compositions for mat materials obtained by coextrusion of a linear carboxylic polyester with acid value between 20 and 50 mg of KOH and an acrylic polymer containing from 5 to 30% of glycidic methacrylate are claimed.

WO 89/06674 of the same applicant describes mat films obtained by the "DRY BLEND" mixture of powder paints consisting of binder systems different from each other for crosslinking and reactivity.

The subsequent WO 89/10949 of the same applicant describes the opportunity of continuous production of these paints by extruding them parallelly and hot-mixing them after extrusion.

All the aforesaid systems as a binder composition of paints use saturated carboxylic or hydroxyl polyesters, isocyanic hardeners, glycidic acrylic or carboxylic or hydroxylic resins and other various hardeners. All resins need temperatures above 140°C and time above ten minutes and thereafter these paints can be applied only on heat-resistant supports because the heat delivered while the paint is melting and crosslinking is largely absorbed also by the support which can be deformed or deteriorated.

In view of developing new binder systems for powder paints able to meet market requirements such as time and baking temperature reduction and the opportunity of painting also thermosensitive supports we have devoted a great part of our research in order to both find out application methods meeting these requirements as claimed in our Italian patent application MI 96A 001728 concerning a method of hot air application of thermomeltable powder polymers and obtain unsaturated powder polymers to be used as hardenable paints by means of radiations or catalysts soon after the application and melting. As it turns out in Italian patent application MI 96A 001097 we obtained as much as we had set but the

problem relating to manner of obtaining mat powder paints derived from these unsaturated products was not solved.

Relying on previously gained experience, which has been described in aforesaid WO 89/06674 and WO 89/10949 we have tried to carry out mat paints using these methods, but because of the similitarity of these unsaturated polymers and crosslinking systems at the beginning the results have been not very encouraging.

Then continuing our research we found out that the use of a crystalline unsaturated polyester by its own as a binder gives a semiglossy paint and that because of the the use of technology described in aforesaid prior art namely by mixing two paints, one composed of an unsaturated crystalline polymer and the other of an amorphous unsaturated polymer, the resultant paint is clearly matter.

Moreover we found out that in addition to the amorphous or crystalline condition the difference of amount of double bonds contained in the two binder systems also increases the mat appearance of the produced paint, and this fact occured also for pairs of systems which were only amorphous and only crystalline.

As a consequence, according to the present invention powder paints, which are satin or mat by using binder systems containing unsaturated polymers, can be obtained by dry blending (dry blend) or coextruding two or more compositions different from each other both for physical appearance (amorphous or crystalline) and for unsaturated functional groups (the one with a few and the other with a lot) by means of two or more adiacent extruders with a single exit nozzle. A maximal opacity is obtained with a 1:1 ratio by weight between the two mixtures.

After a simple melting the applied system was already mat and it was surprisingly noted that crosslinking emphasized the film opacity (gloss reduction).

In order to better illustrate this invention some examples not limiting the invention are given hereinafter.

Description of the unsaturated polymers and the additives used in illustrative examples of the invention:

Unsaturated amorphous polyester 03490 produced by Vianova Resins with Tg ~ 46°C and unsaturation degree of equivalent weight ~ 650.

Amorphous unsaturated polyester Viaktin VAN 1743 of Vianova Resins with Tg ~ 46°C and unsaturation degree of equivalent weight ~ 770.

Amorphous unsaturated acrylate polyurethane 03546 of Vianova Resins with Tg ~

52°C and unsaturation degree of equivalent weight ~ 380.

Crystalline unsaturated polyester 03453 of Vianova Resins with melting point 85 ~ 100°C and unsaturation degree of equivalent weight ~ 90.

Crystalline unsaturated polyester 03489 of Vianova Resins with melting point 130 ~ 140°C and unsaturation degree of equivalent weight ~ 550.

Examples.

In the formulations all parts are by weight unless otherwise specified.

Example 1

Viaktin VAN 1743	917
Additol VXL 9824	50
Benzoin	3
Photoinitiator	30

Example 2

Viaktin 03546	917
Additol VXL 9824	50
Benzoin	3
Photoinitiator	30

Example 3

Viaktin 03490	917
Additol VXL 9824	50
Benzoin	3
Photoinitiator	30

Example 4

Viaktin 03435	917
Additol VXL 9824	50
Benzoin	3
Photoinitiator	30

Example 5

Viaktin 03489	917
Additol VXL 9824	50
Benzoin	3
Photoinitiator	30

Example 6

Viaktin VAN 1743	767
Additol VXL 9824	50
Benzoin	3
Photoinitiator	30
TiO_2	150

Example 7

Viaktin 03546	767
Additol VXL 9824	50
Benzoin	3
Photoinitiator	30
TiO_2	150

Example 8

Viaktin 03490	767
Additol VXL 9824	50
Benzoin	3
Photoinitiator	30
TiO_2	150

Example 9

Viaktin 03453	767
Additol VXL 9824	50
Benzoin	3
Photoinitiator	30
TiO_2	150

Example 10

Viaktin 03489	767
Additol VXL 9824	50
Benzoin	3
Photoinitiator	30
TiO_2	150

Example 11

Viaktin VAN 1743	767
Additol VXL 9824	50
Benzoin	3
Peroxide	30
TiO_2	150

Example 12

Viaktin 03546	767
Additol VXL 9824	50
Benzoin	3
Peroxide	30
TiO_2	150

Example 13

Viaktin 03490	767
Additol VXL 9824	50
Benzoin	3
Peroxide	30
TiO_2	150

Example 14

Viaktin 03453	767
Additol VXL 9824	50
Benzoin	3
Peroxide	30
TiO_2	150

Example 15

Viaktin 03489	767
Additol VXL 9824	50
Benzoin	3
Peroxide	30
TiO_2	150

Example 16

Viaktin VAN 1743	632
Additol VXL 9824	50
Benzoin	3
Photoinitiator	15
Filler	150
TiO_2	150

Example 17

Viaktin 03546	617
Additol VXL 9824	50
Benzoin	3
Photoinitiator	30
Filler	150
TiO_2	150

Additol VXL9824: stretching master agent, trademark registered by Vianova Resins.

Photoinitiator: e.g. Irgacure 651 and Irgacure 1800 registered by Ciba.

Peroxide: e.g. Dicumyl-peroxide

Formulations of the above described examples were extruded by means of twin screw extruder under the following conditions:

- T(°C): 80-100-100
- Al (%): 20
- RPM: 300

Extrudate was cooled, micronized and sieved (<125 μ). Powder paints so obtained were applied with a corona gun and the film was hardened over a IR-UV dynamic oven with ten IR lamps 230 V/800 W and two UV lamps at 80 W/cm.

For approval tests sheet metals of Al and wood panels MDF were used.

Blends at 1: 1 ratio by weight are carried out between the paints formulated (dry blend) in each mixture.

For paints containing peroxydic initiator traditional baking and only infrared cooking are carried out.

UNSATURATED MAT DRY BLEND:

Transparent Systems

Blends	Gloss 20°	Gloss 60 °
E1/E4	37 (41)	70(75)
E2/E4	65(70)	119(122)
E3/E4	28(21)	54(42)
E1/E5	100	137
E2/E5	87	133
E3/E5	103	141
E4/E5	17	34

Pigmented systems

Blends	Gloss 20°	Gloss 60 °
E9/E6	6	31
E9/E7	13	50
E9/E8	14	49
E10/E6	19	57
E10/E7	28	70
E10/E8	14	55
E10/E9	5	21
E16/E17*	16	54

*: application with hot air

Pigmented systems with peroxide

Blends	Gloss 20°	Gloss 60 °
E14/E11	5	30
E14/E12	6	36
E14/E13	9	41
E14/E15	4	24
E15/E11	18	57
E15/E12	8	43
E15/E13	6	36

CLAIMS

1. Powder paint compositions which are mat or satin hardenable by means of radiations or radical catalysts comprising unsaturated polymers as a binder characterized in that said compositions consist of physical blends, but not intimately homogenized, obtained by mixing, in a molten or hot or cold state, two or more powder paints each one comprising an unsaturated polymer different for "amorphous or crystalline" appearance and for amount of unsaturated functional groups.

2. Compositions according to claim 1 characterized in that before being mixed one paint comprises a crystalline unsaturated polymer with an amount of functional groups different from the other paint containing an amorphous unsaturated polymer.

3. Compositions according to claim 1 characterized in that the paints can be hardened by means of radiations with electron beams or photoinitiators, microwaves or radical catalysts.

4. Compositions according to claim 1 characterized in that pigments, fillers and various additives used with traditional powder paints are comprised besides the binder.

5. Process for the production of compositions according to any one of the previous claims characterized in that extruded paints can be blended separately in the molten state by molten of two adiacent or parallel extruders having either two adiacent nozzles or a single nozzle with separate extrusion chambers; or can be hot-mixed joining the extrudates which are still hot by means of a calender or quench bath; or can be cold-mixed.

6. Substrates painted even partially by the compositions of claim 1.

7. Process for the application of compositions according to any one of Claims 1-5, characterized in that paint compositions not intimately mixed (dry blend) are applied through traditional methods (corona or tribo) and/or hot air.

8. Process for the application of the compositions of claim 1 and/or 2 characterized by being mixed at different ratios according to the desired opacities and effects.

INTERNATIONAL SEARCH REPORT

Internati. Application No
PCT/EP 98/03439

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D167/06 C09D175/16 C09D5/03

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09D

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 98 18862 A (UCB, S.A.) 7 May 1998 see claims 1-30	1-8
A	EP 0 098 655 A (DSM RESINS) 18 January 1984 see claims 1-8	1-8
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A	DE 23 62 397 A (BASF AG) 19 June 1975 see claim 1	1-3
A	US 5 110 846 A (FARRONATO ET AL.) 5 May 1992 see claims 1-5	1,5

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	DE 22 47 779 A (SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ B.V.) 5 April 1973 see page 8, line 27 - page 9, line 5; claims 1-5	1

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