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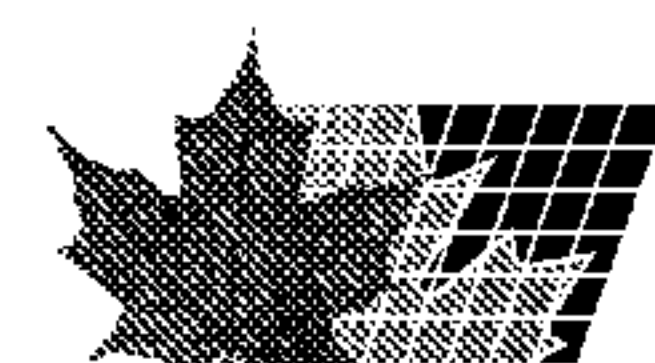
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(57) **Abrégé/Abstract:**

The invention relates to dry polymer pigments, particularly to plastic pigments applicable in dry form that may be used in a dry coating method of paper and board, and to a method for producing polymer pigments applicable in dry form. The plastic polymer pigment applicable in dry form comprises plastic pigment particles wherein the size of individual particles is from 10 to 2000 nm, the dry matter content of the plastic polymer pigment being from 85 to 100 wt% of the polymer pigment, and the individual plastic pigment particles form agglomerates having a size from 1 to 500 µm.



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(54) Title: POLYMER PIGMENT APPLICABLE IN DRY FORM

(57) Abstract: The invention relates to dry polymer pigments, particularly to plastic pigments applicable in dry form that may be used in a dry coating method of paper and board, and to a method for producing polymer pigments applicable in dry form. The plastic polymer pigment applicable in dry form comprises plastic pigment particles wherein the size of individual particles is from 10 to 2000 nm, the dry matter content of the plastic polymer pigment being from 85 to 100 wt% of the polymer pigment, and the individual plastic pigment particles form agglomerates having a size from 1 to 500 µm.



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Polymer pigment applicable in dry form

5 The present invention relates to dry polymer pigments, particularly to plastic pigments applicable in dry form which pigments may be used in a dry coating method of paper and board, and to a method for producing polymer pigments applicable in dry form. This invention is further directed to a method for dry coating of paper and board with a polymer pigment by ionic blasting, and to dry coated
10 paper and board.

Synthetic plastic pigments are increasingly used in coating of paper, to partly or totally replace conventional inorganic pigments, such as calcium carbonate and kaolin. Plastic pigments are commonly used as aqueous dispersions, i.e. latexes,
15 with dry matter contents varying between 20 and 60 wt%. Synthetic plastic pigments may either have a solid core, or they may be hollow. Chemically these plastic pigments are based on polyacrylate, polymethacrylate, or polystyrene, or the copolymers thereof and further pigments based on urea-formaldehyde and melamin-formaldehyde are used. A plastic pigment, particularly a hollow particle
20 pigment endows the product made thereof with opacity and brightness. A problem related to the aqueous dispersions of plastic pigments is, however, limited storage stability, and solid polymer particles tend to settle on the bottom of the container during extended storage. Moreover, plastic pigments do not usually tolerate freezing and thawing, and the polymer pigment also coagulates easily when
25 freezing. Accordingly, the storage temperature restricts the storage thereof. In addition, the aqueous dispersions of plastic pigments are liable to microbial growth. For these reasons, a plastic pigment easily turns into a useless product. The water content of the aqueous dispersions of plastic pigments being normally from 40 to 80 %, significant extra expenses are caused by the transportation of
30 water.

Coating of paper is conventionally carried out by applying on a paper web a pigment dispersion or paste, typically containing from 30 to 40 % of water. Drying of the coated paper is an energy consuming process, since the water must be removed with for instance IR-dryers. This water pollutes the environment, and must accordingly be treated carefully before releasing it into surface waters. Moreover, the coating line of a paper machine with its paste kitchen is a relatively large unit requiring lots of space, and further, the coating line of a paper machine is a very significant investment.

10 Recently, a new dry coating method by ionic blasting that saves water, energy, and raw materials has been developed for paper coating. Dry coated paper web needs no drying, and thus no energy is consumed by drying. Further, such a paper machine requires less space than a conventional one. In the new dry coating method, a dry pigment is applied onto a paper web using a particle transfer technique based on ionic blasting. This method also utilizes the binding properties of small particles. By transferring the coating material in the form of very fine particles onto the surface of the web using ionic blasting, the particles may be made to bind to paper fibers and to each other directly, without an extra binder. In this method, the paste is applied onto the web without contacting it, by means of ionic blasting provided by high voltage, wherein the particles are charged by the ions formed by corona discharge. Thereafter, an electric field transfers the charged particles onto the paper web. Many quality properties of the paper are also improved, since the paper substrate is no longer wetted and redried. The above teaching suggests that there is an evident need for a synthetic plastic pigment, applicable in dry form, that may particularly be used in the new dry coating method of paper.

An object of the present invention is a plastic polymer pigment applicable in dry form, a method for producing such a plastic polymer pigment, applicable in dry form, and the use of a plastic polymer pigment, applicable in dry form, in a method for dry coating of paper or board. In addition, another object of the inven-

tion is a method for dry coating of paper or board by ionic blasting with a polymer pigment, and dry coated paper or board.

The characteristic features of the plastic polymer pigment, applicable in dry form, the method for producing such a plastic polymer pigment, applicable in dry form, the use of a plastic polymer pigment, applicable in dry form, in a method for dry coating of paper or board, the method for dry coating of paper or board by ionic blasting with a polymer pigment, and the dry coated paper or board of the invention are presented in the claims.

In the present invention, it was discovered that paper and board may be coated with a dry coating method by using plastic polymer pigments applicable in dry form. Plastic polymer pigments may be dried with a suitable method, preferably by using spray drying technique to produce finely divided pigment powder. Suitable polymer pigments are at least plastic pigments based on polystyrene, polyacrylate, and polymethacrylate, poly(styrene-acrylate)copolymers, plastic pigments based on melamin-formaldehyde and urea-formaldehyde, or combinations thereof. The plastic pigment is dried from an aqueous dispersion having a dry matter content from 1 to 85 wt%, preferably from 5 to 60 wt%, by weight. The particle size of the plastic pigment to be dried is in the range of 10 – 2000 nm, preferably 150 – 1000 nm. With respect to the surface structure, the plastic pigment to be dried is hydrophobic or hydrophilic, and it may contain various reactive groups allowing the modification of its properties. The bulk density of the plastic pigment to be dried is between 100 and 2000 g/l, and the glass transition temperature thereof is from 80 to 160 °C. With respect to its structure, the plastic pigment may be either hollow or solid. By polymerizing different relative amounts of monomer starting materials, shell hardness, softening temperature, binding power, abrasion resistance, printability, and of course, material costs of the pigment particle may be controlled. The drying is carried out with any suitable drying method that produces dry and sufficiently finely divided pigment powder, preferably by means of spray drying. In a conventional spray drying method, the polymer dispersion is

pumped to a nozzle of a cyclone. The nozzle may be stationary or rotating, and the dispersion is quickly heated therein by means of hot air, having a temperature from 150 to 250 °C. The dispersion is then blown into the cyclone, wherein drop-lets are formed and at the same time, water is immediately evaporated. Typically,
5 the temperature in the cyclone is in the range of about 80 – 100 °C. The dried pigment powder is collected in the receptacle of the cyclone. Any suitable spray drying apparatus may be used as the spray dryer.

The properties of the plastic pigment may further be modified in several ways,
10 both chemically and physically. By adjusting the molecular weight distribution of the plastic pigment, rheological properties thereof may be controlled, including:
a) the viscosity in the softening range,
b) the elasticity that lowers the penetration and prevents excessive flowing, and
c) the degree of crosslinking that influences the elasticity and viscosity.

15

Quick heating and compressing steps of the dry coating method also have a beneficial effect on the rheological and thermal properties of the plastic pigment. The thermal resistance of the plastic pigment may preferably be improved with a melamin-formaldehyde or urea-formaldehyde treatment, the melting temperature
20 may be modified, pressure resistance may be improved, and charging properties and printability may be adjusted as desired.

Both solid and liquid adjuvants and additives may be added to the dispersion before, and in some cases even after spray drying. Granulating additives, adhesives,
25 optical brighteners, latex, agent that modify the electrical properties, and other conventional additives for paper and board may be added to the dispersion. Suitable granulating additives include carboxy methyl cellulose (CMC), polyvinyl alcohol (PVA), styrene butadiene latex (SBS), polyethylene wax (PE), the suitable amount of an additive being from 0,5 to 5 wt% of the dispersion. Suitable binders
30 of the coating include SBS and PVA. Suitable additives may be used to improve the brightness of the paper or board. Antimicrobial additives may be used in the

manufacture of antibacterial paper or liquid packaging board. Further, inorganic additives such as kaolin, talc, titanium dioxide, satin white, precipitated calcium carbonate (PCC), ground calcium carbonate (GCC) or like may be used, beneficially influencing the properties of the plastic pigment, including chemical, physical, printing and economic features thereof. These additives may also be used to adjust the charging, binding, and powdering properties of the plastic pigment, as well as the handling properties thereof when transporting and transferring the material to the coating unit.

The drying of the plastic pigment either as such or combined with additives results in finely divided pigment particle agglomerates in dry form, with a particle size between 1 and 500 μm , the dry matter content thereof being in the range of 85 – 100 %. These pigment particle agglomerates consist of individual spherical pigment particles bonded together with electrostatic forces. These particles may be either hollow or solid.

Further, the dried plastic pigment powder may optionally be treated with a refiner wherein the structure is partly crushed thus increasing porosity and opacity. By treating dry pigment in a high-power refiner, the electrical properties of the pigment are changed, which affects the binding of the pigment to the paper web.

Advantages of the dry plastic polymer pigment include the ease of transportation and storage, and resistance to temperature changes.

A plastic pigment for instance affects the printing properties as follows:

- a) printing quality is improved since the gloss and smoothness are improved and are more uniform throughout the surface,
- b) plastic pigment is favourable to the setting and stability of the printing ink, since the surface is not too porous and the ink does not penetrate too deeply into the paper,

- c) since the surface of the plastic pigment particles is not porous, the printing ink will not spread too much, or form blurred outlines, and
- d) with the plastic pigments, sufficient surface strength for printing is attained.

5 The hollow structure yields the particle elasticity under compression, and thus the surface of the coating will be compressed more than its middle layer during calendaring or like finishing step, and binding. Moreover, the hollow core of the particle endows the coating with opacity as the ability to scatter light improves, and a wide particle size distribution results in dense packing that leads to superior hiding power. The optical properties of the product depend on the size, shape, and topology of the pigment particles and the distribution thereof, allowing the adjustment of gloss, smoothness, opacity, brightness and hiding power. In addition, a polymer pigment to be stored in a dry form is not liable to microbial contamination, for instance to bacterial contamination in contrast to prior aqueous dispersions. The shape of the pigment being spherical, the particle may be compressed without losing its hollow structure. The adjustment of the refractive index of the plastic pigment between 1.3 and 1.65, preferably between 1.6 and 1.65, results in a significant deviation from the refractive index of air (being 1), thus increasing the scattering power and providing the brightness with a slight bluish shade. A respective effect may be provided by adjusting the hollow volume between 10 and 80 %. Since the drying process is fast, the surface properties of the particle are not altered during this short exposure to high temperatures. Spray drying may change the electrical properties of the particles, thus improving the formation of agglomerates. A pigment with a narrow size distribution is charged more uniformly than a pigment with a wide size distribution. Hollow polymer pigments generally increase the stiffness of paper or board, and they have a high hiding power. The plastic pigment also acts as a binder for an inorganic pigment thus improving the binding thereof, and the smoothness of the coating. The hollow agglomerate structure of the plastic pigment is retained in the coating, the plastic pigment increasing the binding power of other coating materials. The plastic pigment may improve the opacity of coating blends by preventing the agglomeration of mineral

components and by uniformly distributing the pigment. The structure and the large scattering area of the plastic pigment particles and agglomerates are favorable for attaining a high opacity and a sufficient brightness in a dry coating layer. In case of plastic pigments, the amount of a polymer acting as an adhesive needed for a known pigment volume is lower. With the plastic pigment, the shade of the coated product may be adjusted as desired.

The plastic pigments may be considered acting as additives for finishing the paper surface, since they make the surface more adjustable. Thus the undesired compression of the paper substrate under pressure decreases.

In addition to the high bulk and stiffness attained, the weight of the coated paper may be decreased by using pigments with a lower density. By providing the desired coating thickness with a lighter layer, the fiber proportion of the paper substrate may respectively be increased, thus increasing the strength of the paper. Accordingly, a paper coated with a plastic pigment is lighter than conventional paper.

Since a high quality surface is provided at lower treatment temperatures and pressures, the calender cylinders are worn less. The efficiency of the coating unit may respectively be improved by increasing the speed.

In addition, an advantage of the finely divided plastic pigment coating is the fact that it shrinks less than film forming latexes of prior art after thermal treatment and binding.

Various traditional methods used in paper processing technology may be replaced with this novel dry coating method using the polymer pigment applicable in dry form, selected according to the application.

Further, the use of the plastic pigment applicable in dry form provides several advantages in dry coating in comparison to conventional inorganic pigments, including the fact that the plastic pigments softens at about 100 – 120 °C, and thus the plastic pigment applied is well bound to the paper substrate during calendering, typically carried out above the glass transition temperature of the plastic pigment. Because of this softening, no extra binder is needed. If necessary, the composition of the coating may be tailored as desired by using other additives and components with the plastic pigments, thus making a wide variety of plastic pigments available. Moreover, the properties of the plastic pigments may be chemically modified and tailored as desired. The paper coated with the plastic pigment may be recycled by burning, since it does not contain any nonburning inorganic matter, or the plastic pigment may be chemically separated from the paper.

The invention will now be illustrated with the examples without wishing to limit the scope thereof.

Example 1

A plastic pigment, applicable in dry form, was prepared by spray drying from a plastic pigment dispersion based on polyacrylate and polystyrene, having a dry matter content of 30 %, by weight. The temperature of the nozzle of the cyclone was 160 °C, and the temperature in the cyclone was 80 °C. A rotating nozzle was used in the cyclone, rotating at the speed of 30 000 rpm. The particle size of the dry plastic pigment obtained was 60 µm, the density was 0.26 g/cm³, and the water content was 0.05 %, by weight.

The paper substrate used was a yellowish, rather coarse paper from mechanical pulp, having following characteristics:

grammage	about 70 g/m ²
thickness	120 – 124 µm
Bendtsen smoothness	4.5 – 5 µm

tearing resistance	400 mN
burst index	2.0
tensile strenght	machine direction 50 kN/m
	cross direction 25 kN/m
opacity	94.1
brightness	90.1
gloss (75°)	8

The plastic pigment powder was applied onto the paper substrate by ionic blasting. After application, the powder was irreversibly bound to the paper by thermal compression. The temperatures used in binding were: 100 °C, 120 °C, 150 °C,
5 170 °C and 200 °C.

Linear loads of the calender used at control points were 3.4 kN/m, 6.8 kN/m and 13.7 kN/m. The total number of the control points made using this plastic pigment was 15. In addition, the binding of the pigment with IR heating was studied, the
10 temperature being in this case about 110 °C.

The tensile strenght, the tearing and burst resistances, smoothness, gloss, opacity, and brightness of the coated paper were tested after thermal compression.

15 The properties were as follows:

- The grammage of the paper increased only by about 10 – 15 g/m².
- The thickness of the paper increased even by 10 – 20 µm.
- The smoothness of the paper improved by about 2.5 – 3 µm.
- The opacity and brightness increased significantly compared to the paper substrate at the temperature range of 100 – 150 °C. Above 150 °C the opacity and
20 brightness were comparable to those of the paper substrate.
- The tensile strenght increased on an average by 5 kN/m, the effect being strongest at high temperatures.

- The gloss increased with increasing temperatures. At lower temperatures, the gloss was lower than that of the paper substrate, and at higher temperatures the value of the gloss was approximately 15 % higher.

5 According to the IGT testing method, high printability values were obtained by binding the coating at a low temperature (100 °C) with a high linear load (13.7 kN/m), or by using IR heating (110 °C) with a low linear load (3.4 kN/m).

Example 2

10

A plastic pigment applicable in dry form was prepared as described in Example 1. The temperature of the nozzle was 210 °C. The particle size of the dry plastic pigment obtained was 70 µm, its density was 0.30 g/cm³, and the water content was 0.05 %, by weight.

15

The paper substrate was coated as in Example 1.

After the thermal compression, the properties of the paper were as follows:

- The grammage of the paper increased only by about 10 g/m².
- 20 • The thickness increased on an average even by 20 µm, at higher temperatures, the thickness of the coated paper decreased.
- The smoothness of the paper was improved by about 1.5 µm, and the smoothness of the coated paper improved as the temperature rose.
- The opacity increased significantly compared to the paper substrate at the temperature range of 100 – 150 °C. Above 150 °C, the opacity was comparable to that of the paper substrate.
- 25 • The brightness of the coated paper attained that of the paper substrate at temperatures above 150 °C.
- The tensile strenght of the coated paper was on an average by 5 - 10 kN/m higher than that of the paper substrate, and the tensile strenght improved as the temperature rose.
- 30

- IR heating improved the tensile strenght on an average by 5 kN/m.
- The gloss of the paper coated at lower temperatures was comparable to that of the paper substrate, and as the temperature rose, the gloss improved significantly, being finally 20 % higher than that of the paper substrate.

5

According to the IGT testing method, high printability values were obtained by binding the coating at a low temperature (100 °C) with a high linear load (13.7 kN/m), or by using IR heating (110 °C) with low linear load (3.4 kN/m).

10 Example 3

A plastic pigment applicable in dry form was prepared from a plastic pigment dispersion of polyacrylate-polystyrene, added with 10 %, by weight, of calcium carbonate (PCC). The drying was carried out as in Example 1. The particle size
15 was 30 µm, and the water content was 0,05 %, by weight.

The coating was carried out as in Example 1.

After the thermal compression, the properties of the paper were as follows:

- 20 • The grammage of the paper was by 15 – 20 g/m² higher than that of the paper substrate.
- The thickness of the paper increased even by 25 – 35 µm.
- The smoothness improved by 1.0 – 2.5 µm as the temperature rose.
- The opacity decreased as the temperature rose, being, however, higher than
25 that of the paper substrate regardless of the temperature.
- The brightness was some percent higher than that of the paper substrate. As the temperature rose to its maximum value, the brightness reached the value of the paper substrate.
- The tensile strenght of the coated paper increased on an average by 5 kN/m.

- At lower temperatures, the gloss of the coated paper was lower than that of the paper substrate. As the temperature rose, the gloss was approximately 10 % higher than that of the paper substrate.

5 According to the IGT testing method, printability values were high for a sample bound at a high temperature (200 °C) using a medium linear load (6.8 kN/m).

Example 4

10 A plastic pigment, applicable in dry form, was prepared from a plastic pigment dispersion of polyacrylate-polystyrene, added with 10 %, by weight, of titanium dioxide. The drying was carried out as in Example 1. The particle size was 27 µm, and the water content was 0,05 %, by weight.

15 The dry coating was carried out as in Example 1.

After the thermal compression, the properties of the paper were as follows:

- The grammage of the paper increased by 40 – 50 g/m².
- The thickness increased by 50 µm.
- 20 • The smoothness of the coated paper improved by about 1.5 – 2.5 µm.
- The temperature had little effect on the opacity. The opacity of the coated paper was 3 % higher than that of the paper substrate.
- The opacity of an IR heated coated paper was 4 % higher than that of the paper substrate.
- 25 • The brightness decreased with increasing temperatures, reaching however always higher values than those of the paper substrate, even as IR heating was used.
- The tensile strength decreased with increasing temperatures. The lowest value thereof was however higher than that of the paper substrate, being on an average by 5 - 10 kN/m higher.
- 30 • With IR heating, the tensile strength improved by 5 kN/m.

- The gloss of the coated paper increased by about 10 %.
- The gloss of the IR heated coated paper was higher than that of the paper substrate at low pressures.

5 **Example 5**

In examples 1 – 4, the coated paper substrates were studied with SEM and stereo microscopy. The images obtained revealed that the resulting surface was very smooth due to the dense packing of the pigment agglomerates deforming under pressure.

Amended Claims

1. A plastic polymer pigment, applicable in dry form, **characterized** in that the plastic polymer pigment comprises plastic pigment particles, the size of individual particles being from 10 to 2000 nm, the individual plastic pigment particles being hollow, the dry matter content of the plastic polymer pigment being from 85 – 100 %, by weight, and the plastic polymer pigment comprises a polymer based on polystyrene, polyacrylate, poly(styrene-acrylate), or polymethacrylate, or a polymer based on urea-formaldehyde or melamine-formaldehyde, or combinations thereof.
2. A plastic polymer pigment of claim 1, applicable in dry form, **characterized** in that the individual plastic pigment particles form agglomerates having a size from 1 to 500 μm .
3. A plastic polymer pigment of claim 1 or 2, applicable in dry form, **characterized** in that the refractive index of the plastic polymer pigment is between 1.3 and 1.65, preferably between 1.6 and 1.65.
4. A plastic polymer pigment of any of claims 1 - 3, applicable in dry form, **characterized** in that the individual plastic pigment particles are bonded together with electrostatic forces to form agglomerates.
5. A plastic polymer pigment of any of claims 1 - 4, applicable in dry form, **characterized** in that the plastic polymer pigment further comprises inorganic pigment.
6. A plastic polymer pigment of any of claims 1 - 5, applicable in dry form, **characterized** in that the plastic polymer pigment further comprises granulating agent.

7. A plastic polymer pigment of any of claims 1 - 6, applicable in dry form, **characterized** in that the plastic polymer pigment further comprises additive(s) used in the production of paper or board.
- 5 8. A plastic polymer pigment of any of claims 1 - 7, applicable in dry form, **characterized** in that the structure and the large scattering area of the plastic pigment particles and agglomerates are favourable for attaining a high opacity and a sufficient brightness in a dry coating layer, and the shade of the coated product is adjusted as desired with the plastic polymer pigment.
- 10 9. A plastic polymer pigment of any of claims 1 - 8, applicable in dry form, **characterized** in that the properties needed in dry coating with the plastic polymer pigment, including grounding and charging properties, adhesion to paper, ease of transfer with ionic blasting, and stability of the finely divided form in the
- 15 process may be adjusted as desired.
10. Use of the dry plastic polymer pigment according to any of claims 1 - 9 in a method for dry coating of paper or board.
- 20 11. Use of claim 10, **characterized** in that the dry coating method is based on ionic blasting.
12. A method for dry coating of paper or board, **characterized** in that a paper or board web is coated by ionic blasting with a pigment or pigment mixture in the
- 25 form of small particles, this pigment containing plastic polymer pigment wherein the particle size of the individual particles is from 10 to 2000 nm, the dry matter content of the pigment being from 85 to 100 wt%.
13. A method of claim 12, **characterized** in that the individual plastic pigment
- 30 particles form agglomerates having a size from 1 to 500 μm .

14. A method of claim 12 or 13, **characterized** in that the individual plastic pigment particles are hollow.
15. A method of claim 12 or 13, **characterized** in that the individual plastic
5 pigment particles are solid.
16. A method of any of claims 12 - 15, **characterized** in that the refractive index of the plastic polymer pigment is between 1.3 and 1.65, preferably between 1.6 and 1.65.
- 10 17. A method of any of claims 12 - 16, **characterized** in that the individual plastic pigment particles are bonded together with electrostatic forces to form agglomerates.
- 15 18. A method of any of claims 12 - 17, **characterized** in that the plastic polymer pigment comprises a polymer based on polystyrene, polyacrylate, poly(styrene-acrylate), or polymethacrylate, or a polymer based on urea-formaldehyde or melamine-formaldehyde, or combinations thereof.
- 20 19. A method of any of claims 12 - 18, **characterized** in that the plastic polymer pigment is modified with melamine-formaldehyde or urea-formaldehyde, or with combinations thereof.
- 25 20. A method of any of claims 12 - 14, **characterized** in that the plastic polymer pigment further comprises binder.
21. A method of any of claims 12 - 20, **characterized** in that the plastic polymer pigment further comprises inorganic pigment.
- 30 22. A method of any of claims 12 - 21, **characterized** in that the plastic polymer pigment further comprises granulating agent.

23. A method of any of claims 12 - 22, **characterized** in that the plastic polymer pigment further comprises additive used in the production of paper or board.

5 24. A method of any of claims 12 - 23, **characterized** in that the structure and the large scattering area of the plastic pigment particles and agglomerates are favourable for attaining a high opacity and a sufficient brightness in a dry coating layer, and the shade of the coated product is adjusted as desired with the plastic polymer pigment.

10

25. A method of any of claims 12 - 24, **characterized** in that the properties needed in dry coating with the plastic polymer pigment, including grounding and charging properties, adhesion to paper, ease of transfer with ionic blasting, and stability of the finely divided form in the process may be adjusted as desired.

15

26. Dry coated paper or board, **characterized** in that it contains a plastic polymer pigment of any of claims 1 - 9 applicable in dry form.