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(54) **THERMOPLASTIC ARTICLE WITH A PRINTABLE MATTE SURFACE**

THERMOPLASTISCHER ARTIKEL MIT EINER BEDRUCKBAREN MATTEN OBERFLÄCHE  
ARTICLE THERMOPLASTIQUE A SURFACE MATE IMPRIMABLE

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**EP 1 768 806 B9**

**Description**FIELD OF THE INVENTION

**[0001]** This invention relates to thermoplastic articles having printable matte surfaces. In particular, the printable matte surface is achieved by blending inorganic particles, and especially silica particles, having a specific particle size and particle size distribution into the thermoplastic.

BACKGROUND OF THE INVENTION

**[0002]** Thermoplastics are useful in the manufacture of many articles since they can be easily molded into a variety of shapes, they form hard and durable articles, and there is excellent flexibility for designs and fabrications at a competitive cost.

**[0003]** Controlling the gloss level of polymeric articles is important for many applications. For some polymeric materials such as acrylics, high gloss articles can be readily obtained, but low gloss or matte articles that retain their gloss levels upon subsequent processing (e.g. thermoforming) are more difficult to obtain. Often other properties, such as surface roughness and mechanical toughness are altered significantly by the matting process.

**[0004]** One method for obtaining matte thermoplastic articles involves the mechanical embossing of a pattern onto an article, such as by sand blasting or surface pattern fabrication. Articles made by this approach can have a low-gloss surface but typically do not maintain their gloss levels upon subsequent processing such as thermoforming or lamination onto a substrate.

**[0005]** Another approach for obtaining a matte finish involves the deposition of a coating or paint onto an article. A matting agent in the coating formulation provides the low-gloss surface to the article. However, this approach is not cost effective because of the need to cure and dry the coating.

**[0006]** Still another approach relies upon the modification of the thermoplastic resin by the addition of inorganic or organic particle of the appropriate size and refractive index.

**[0007]** Organic particles have been used to reduce the gloss on the surface of a thermoplastic, as described in European patent EP 1022115, US Patent Number 5,346,954, and JP 2001081266. The use of organic polymeric particles produces a matte finish, but they can be difficult to make and therefore expensive. Furthermore, the handling of fine powder of organic polymer is more likely to create conditions for dust explosions than in the case of handling some silica powders.

**[0008]** Inorganic fillers have also been used to incorporate a matte finish on thermoplastic articles. Unfortunately, these inorganic particles, such as, barium sulfate, calcium carbonate, titanium dioxide, silica, etc. are normally difficult to disperse evenly in polymer matrix material. They also tend to reduce greatly the light transmission of the polymer, and do not generate the desired surface texture. Additionally, the filler particles have a tendency to deteriorate physical properties of the polymer.

**[0009]** Fine particles (i. e. less than 15 micrometers) of a copolymer made by an emulsion polymerization process are sometimes added into a plastic matrix to generate a light diffusion effect for display and light panel applications, for example, US patent 5,346,954. However, this type of product tends to soften the polymer matrix and cannot produce the textured surface so often preferred by the end user.

**[0010]** US Patent Number 4,906,676 describes the use of silica or glass particles in thermoplastics for an optical effect. The particles are surface treated with silane compounds to render the surface hydrophobic, and thereby improve the dispersibility of the particle in the thermoplastic matrix.

**[0011]** The disadvantages of current approaches to producing a matte surface on a thermoplastic include: a general loss in mechanical properties (e. g. toughness) ; and introduction of surface roughness. In some applications such as writing or printing onto an article, roughness can be detrimental to image transfer. By choosing particles with a mean diameter < 10  $\mu\text{m}$ , these 2 problems can be minimized. US Patent Number 6,524,694 and Patent application Number 20030175499 describe the use of inorganic particles, such as boron nitride and silicates in extruded thermoplastics. However, in order to obtain good dispersibility a dispersing agent is required and low loading of from 0.01 to 15 weight percent. The presence of a dispersing agent can decrease the mechanical properties of the thermoplastic.

The document US2003/0092789 discloses enhanced scratch resistant coatings using inorganic particles and describes radiation curable coatings of acryl-urethane oligomers, epoxy acrylate oligomers or silicone acrylate oligomers, which contain ceramic spheres to produce a scratch resistant coating.

The document US5308666 discloses a write-on film surface and bags having a write-on stripe. The write on film involves a blend of two incompatible polymers polyethylene or polypropylene with polyisobutylene. Particles are used in the polymer forming the write-on film surface, including silica particles.

**[0012]** Inorganic particles with diameter <1  $\mu\text{m}$ , such as micronized silica, often cause fouling of the melt- processing equipment by accumulation of deposits. Therefore, an optimum range of mean particle diameter exists in order to obtain low gloss and sufficiently low- roughness.

**[0013]** There is a need for a method of providing an advantageous balance of low-gloss, printability, and low migration or "plate-out", without the need for added dispersants or particle surface coatings which add expense and may negatively effect the mechanical properties of the thermoplastic. Presently, there is not a successful plastic product in this market that can be used in a one-step process and provide the properties and appearance needed to replace sand blasted glass material.

**[0014]** Surprisingly it has been found that adding inorganic alkali alumina silica particles, with particle size from 2 to 20  $\mu\text{m}$ , and having a narrow particle size distribution produces a matte finish, without surface roughness. Melt processing or forming (extrusion, lamination, thermoforming) of such materials yields a printable article (film, sheet, laminate) with a low-gloss appearance. The use of silica particles having the particle size and particle size distribution of the invention allows for a higher loading of particles, without the need for a surface treatment or added dispersants.

## SUMMARY OF THE INVENTION

**[0015]** It is an object of the invention to provide a matte or low-gloss finish on a thermoplastic article without high surface roughness. The surface should feel smooth.

**[0016]** It is a further object of the invention to provide a printable surface on a thermoplastic article.

**[0017]** Another object of the invention is to provide an efficient one-step method for adding printability and a low-gloss matte surface to a thermoplastic and articles formed from the thermoplastic.

**[0018]** The objectives of the invention are achieved, in accordance with the principles of a preferred embodiment of the invention, by a thermoplastic article having a matte, printable surface comprising from 15 to 30 percent by weight of inorganic particles. The particles preferably have a mean particle size between 2 and 20  $\mu\text{m}$ .

## DETAILED DESCRIPTION OF THE INVENTION

**[0019]** The invention relates to thermoplastic articles having printable matte surfaces. The printable matte surface is achieved by blending inorganic silica particles, having a specific particle size and particle size distribution into the thermoplastic.

**[0020]** The thermoplastic matrix is ABS terpolymer, ASA copolymer, polycarbonate, polyester, PETG, MBS copolymer, HIPS, acrylonitrile/acrylate copolymer, polystyrene, SAN, MMA/S, an acrylonitrile/methyl methacrylate copolymer, impact modified polyolefins, PVC, impact modified PVC, imidized acrylic polymer, fluoropolymers, polyvinylidenedifluoride (PVDF), PVDF-acrylic polymer blends, acrylic polymer or impact modified acrylic polymer. Preferred thermoplastics are acrylics, including impact modified acrylics, and acrylic copolymers. Especially preferred are polymethylmethacrylate polymers and copolymers.

**[0021]** The inorganic particles useful in the invention have a median particle size of from 2 to 20  $\mu\text{m}$ , preferably from 2 to 12  $\mu\text{m}$ , and most preferably from 3 to 8  $\mu\text{m}$ . It was found that particle sizes over 20  $\mu\text{m}$  produced a surface that was so rough as to make printing difficult. A particle size distribution of the matting agent particles can be evaluated by fractionating particles of different sizes and weigh each fraction. The 95th percentile particle size is the size that 95 percent by weight of the particles are below. In order to minimize the surface roughness, the matting agent has a 95th percentile particle size that is less than 30  $\mu\text{m}$  and most preferably less than 15  $\mu\text{m}$ .

**[0022]** Useful inorganic particles are alkali alumina silica.

**[0023]** In one embodiment, alkali alumina silica particles were those having a mean diameter 4 microns, 95th percentile of particle size distribution is 13  $\mu\text{m}$ .

**[0024]** The inorganic particles are present at from 15 - 30 percent by weight in the thermoplastic article. More preferably the inorganic particles are present at from 16 to 23 percent by weight. When particles were present below 15 percent by weight, the thermoplastic had a gloss level that was too high.

**[0025]** Thermoplastic articles of the invention are formed by means known in the art, such as molding, blow-molding, extrusion, coextrusion, melt cast extrusion, lamination, thermoforming.

**[0026]** The article may be a sheet, a film, a laminate, a rod, cone or other shaped thermoplastic. The thermoplastic may be multi-layered, or a single layer.

**[0027]** The particles may be added to the thermoplastic by methods known in the art. This includes adding the particles at any of the feed ports in an extrusion or molding line. Adding inorganic particles during the extrusion process provides a flexible and low cost process. It also provides a low cost of transitioning from one product to another. The particles are mixed into the thermoplastic in a homogeneous manner by the turbulence of the process.

**[0028]** Alternatively, the particles may be mixed with the thermoplastic near the end of, or after the polymerization process. The particles and thermoplastic are then formed into pellets used as raw materials in extrusion or molding processes. The particles are added to the thermoplastic without the need for dispersants, as required in the art. Homogeneity is obtained by an appropriate profile of mixing and shear stresses in the extrusion process.

**[0029]** In addition to the thermoplastic and inorganic particles, other typical additives may be added to the thermoplastic

composition prior to, or during extrusion and/or molding. These include mold-release agents, impact modifiers, lubricants, dyes and colorants. While the mold release agents and lubricants added to improve processing of the thermoplastic may also act as dispersants, the mold release agents and lubricants are not necessary to ensure good mixing and dispersability of the inorganic particles.

**[0030]** The thermoplastics of the invention have low-gloss, low surface roughness, good light transmittance, and good processability. Uses of such thermoplastics include production of articles such as films, sheets, co-extruded sheets, molded articles. These articles can undergo subsequent process such as printing, decorating, embossing, laminating, etc.

**[0031]** The preferred embodiments of our invention will be exemplified by the following examples. One skilled in the art will realize that minor variations outside the embodiments stated herein do not depart from the spirit and scope of this invention.

#### Examples

**[0032]** Formulations of polymer resin were prepared using the components and proportions described in Table 1. The matting agents used in the examples vary slightly in median particle size and more significantly in the particle size distribution as described in Table 2. The components were mixed by melt extrusion using conditions to obtain homogenous mixtures. The resulting resins were converted into films with thickness = 0.003" (76,2  $\mu\text{m}$ ) by melt extrusion onto a polished roll or rolls. The film samples were evaluated for gloss value and surface roughness.

**[0033]** Gloss values were determined using the BYK Gardner® Micro-Haze Plus gloss meter.

**[0034]** Although the literature claims that matting agents with an average particle size in the range of 1-10  $\mu\text{m}$  is preferred in order to obtain a surface with low roughness, typical matting agents have a broad distribution of particle sizes. Therefore, a significant fraction (>5 wt. %) of the particles are larger than 15  $\mu\text{m}$ . The films of Example 1 - 5 show a range of gloss and roughness behaviors as summarized in Table 3. For applications such as printing onto film, a low roughness and low surface gloss is desired (preferably Gloss Value < 23 at the 60degree-geometry). The use of the matting agent with the narrow particle size distribution (Alkali Alumina Silica #1) yields a film with low toughness and low gloss.

Table 1

Components	Example 1 (Comparative)	Example 2 (Comparative)	Example 3 (Comparative)	Example 4	Example 5
Acrylic Copolymer	80.8%	84.8%	80.8%	80.8%	84.4%
Matting Agent 1				19%	15%
Matting Agent 2			19%		
Matting Agent 1	19%	15%			
Stearyl Alcohol	0.2%	0.02%	0.2%	0.2%	0.2%

Table 2

Matting Agent	Composition	Median Diameter of Particle ( $\mu\text{m}$ )	95 <sup>th</sup> Percentile* ( $\mu\text{m}$ )
1	Alkali alumina silica	4	10
2	Alkali alumina silica	4	18
3	Alkali alumina silica	8	30
*Particle Diameter for which 95% of particles are smaller			

Table 3

Film Sample	Gloss (60 degrees)	Roughness Ranking (1=low roughness, 5= high roughness)
Example 1	16	4
Example 2	22	4
Example 3	19	3
Example 4	19	1
Example 5	26	1

## Claims

1. A thermoplastic article having a matte, printable surface comprising from 15 to 30 percent by weight of inorganic particles having a narrow particle size distribution and a mean particle size of from 2 to 20  $\mu\text{m}$ , preferably from 2 to 12  $\mu\text{m}$ , most preferably from 3 to 8  $\mu\text{m}$ , wherein the 95<sup>th</sup> percentile particle size of inorganic particles is less than 30  $\mu\text{m}$  wherein said inorganic particles comprise alkali alumina silica, and a thermoplastic matrix wherein said thermoplastic is selected from the group consisting of ABS terpolymer, ASA copolymer, polycarbonate, polyester, PETG, MBS copolymer, HIPS, acrylonitrile/acrylate copolymer, polystyrene, SAN, MMA/S, an acrylonitrile/methyl methacrylate copolymer, impact modified polyolefins, PVC, impact modified PVC, imidized acrylic polymer, fluoropolymers, polyvinylidenedifluoride (PVDF), PVDF-acrylic polymer blends, acrylic polymer or impact modified acrylic polymer.
2. The thermoplastic article of claim 1, wherein said thermoplastic is selected from the group consisting of acrylics, including impact modified acrylics, and acrylic copolymers.
3. The thermoplastic article of claim 1 wherein said thermoplastic is a polymethyl methacrylate homopolymer or copolymer.
4. The thermoplastic article of claims 1 to 3 wherein said inorganic particles are selected from the group consisting of silica, talc, alumina, metal carbonates, and mixtures thereof.
5. The thermoplastic article of claims 1 to 3 wherein said inorganic particles are alkali alumina silica.
6. The thermoplastic article of claims 1 to 5 wherein said inorganic particles have a 95<sup>th</sup> percentile particle size of is less than 15  $\mu\text{m}$ .

## Patentansprüche

1. Thermoplastischer Gegenstand mit einer matten, bedruckbaren Oberfläche, umfassend 15 bis 30 Gewichtsprozent anorganische Teilchen mit einer engen Teilchengrößenverteilung und einer mittleren Teilchengröße von 2 bis 20  $\mu\text{m}$ , vorzugsweise 2 bis 12  $\mu\text{m}$ , ganz besonders bevorzugt 3 bis 8  $\mu\text{m}$ , wobei die 95.-Perzentil-Teilchengröße anorganischer Teilchen weniger als 30  $\mu\text{m}$  beträgt, wobei die anorganischen Teilchen Alkalialuminiumoxidsiliciumdioxid umfassen, und eine thermoplastische Matrix, wobei der Thermoplast aus der Gruppe bestehend aus ABS-Terpolymer, ASA-Copolymer, Polycarbonat, Polyester, PETG, MBS-Copolymer, HIPS, Acrylnitril/Acrylat-Copolymer, Polystyrol, SAN, MMA/S, einem Acrylnitril/Methylmethacrylat-Copolymer, schlagzäh modifizierten Polyolefinen, PVC, schlagzäh modifiziertem PVC, imidiertem Acrylpolymer, Fluorpolymeren, Polyvinylidendifluorid (PVDF), PVDF-Acrylpolymer-Mischungen, Acrylpolymer oder schlagzäh modifiziertem Acrylpolymer ausgewählt ist.
2. Thermoplastischer Gegenstand nach Anspruch 1, wobei der Thermoplast aus der Gruppe bestehend aus Acrylharzen einschließlich schlagzäh modifizierten Acrylharzen und Acrylcopolymeren ausgewählt ist.
3. Thermoplastischer Gegenstand nach Anspruch 1, wobei es sich bei dem Thermoplasten um ein Polymethylmethacrylat-Homopolymer oder -Copolymer handelt.

4. Thermoplastischer Gegenstand nach den Ansprüchen 1 bis 3, wobei die anorganischen Teilchen aus der Gruppe bestehend aus Siliciumdioxid, Talk, Aluminiumoxid, Metallcarbonaten und Mischungen davon ausgewählt sind.
5. Thermoplastischer Gegenstand nach den Ansprüchen 1 bis 3, wobei es sich bei den anorganischen Teilchen um Alkalialuminiumoxidsiliciumdioxid handelt.
6. Thermoplastischer Gegenstand nach den Ansprüchen 1 bis 5, wobei die anorganischen Teilchen eine 95.-Perzentil-Teilchengröße weniger als 15 µm aufweisen.

## Revendications

1. Article thermoplastique comportant une surface mate imprimable, comprenant :

de 15 % à 30 % en poids de particules inorganiques ayant une distribution granulométrique étroite et une taille de particule moyenne de 2 µm à 20 µm, préférablement de 2 µm à 12 µm, plus préférablement de 3 µm à 8 µm, la taille de particule des particules inorganiques au 95<sup>ème</sup> percentile étant inférieure à 30 µm, lesdites particules inorganiques comprenant un système alcali-alumine-silice, et une matrice thermoplastique, ledit thermoplastique étant sélectionné dans le groupe comprenant un terpolymère acrylonitrile/butadiène/styrène (ABS), un copolymère acrylonitrile/styrène/acrylester (ASA), un polycarbonate, un polyester, un PETG, un copolymère méthacrylate de méthyle/butadiène/styrène (MBS), un polystyrène antichoc (HIPS), un copolymère acrylonitrile/acrylate, un polystyrène, un copolymère styrène/acrylonitrile (SAN), un copolymère méthacrylate de méthyle/styrène (MMA/S), un copolymère acrylonitrile/méthacrylate de méthyle, des polyoléfines dont la résistance aux chocs a été modifiée, un PVC, un PVC dont la résistance aux chocs a été modifiée, un polymère acrylique imidisé, des fluoropolymères, le difluorure de polyvinylidène (PVDF), des mélanges de PVDF-polymère acrylique, un polymère acrylique ou un polymère acrylique dont la résistance aux chocs a été modifiée.

2. Article thermoplastique selon la revendication 1, dans lequel ledit thermoplastique est sélectionné dans le groupe constitué de composés acryliques, y compris les composés acryliques dont la résistance aux chocs a été modifiée, et les copolymères acryliques.
3. Article thermoplastique selon la revendication 1, dans lequel ledit thermoplastique est un homopolymère ou un copolymère de polyméthacrylate de méthyle.
4. Article thermoplastique selon les revendications 1 à 3, dans lequel lesdites particules inorganiques sont sélectionnées dans le groupe constitué de la silice, du talc, de l'alumine, de carbonates de métaux, et de mélanges de ceux-ci.
5. Article thermoplastique selon les revendications 1 à 3, dans lequel lesdites particules inorganiques sont constituées d'un système alcali-alumine-silice.
6. Article thermoplastique selon les revendications 1 à 5, dans lequel lesdites particules inorganiques ont une taille de particule au 95<sup>ème</sup> percentile qui est inférieure à 15 µm.

**REFERENCES CITED IN THE DESCRIPTION**

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