Impact of Pigments on the Dimensional Stability of Plastics

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Abstract

Shrinkage and Warpage phenomenon are common issues faced by injection molders in the plastics industry. These dimensional stability issues are more prevalent in semi-crystalline polymers such as HDPE. Formulation of organic pigments into semi-crystalline polymers impact the nucleation rates and can lead to further shrinkage and warpage. Dimensional instability with the organic pigments can be can be minimized or eliminated through processing steps as well as through surface treatment of the pigments. This paper will describe the shrinkage and warpage distortions, test methods for determining warpage, and recommend solutions.

Introduction

In injection molded parts, warpage and shrinkage are common dimensional stability issues that molders face while working with semi-crystalline polymers. They are dependent on the type of polymers used, the processing parameters of the polymers, and the presence of certain pigments or additives in the formulation (1).

Shrinkage occurs due to the thermal contraction of the injection molded part during the cooling process in relation to the dimensions of the mold. The degree of shrinkage depends on the crystallinity of the polymers. Shrinkage is more significant in semi-crystalline polymers such as polyolefins in comparison to the amorphous ones such as Acrylonitrile butadiene styrene (ABS) and polystyrene. The shrinkage % of amorphous and semi-crystalline polymers (2) are shown in Table 1. Shrinkage takes place during polymer crystallization, which results in a material with higher degree of order on molecular scale and a higher density at the macroscopic level. The result is a smaller volume and a larger shrinkage with semi-crystalline polymers. Shrinkage will be more heterogeneous throughout complex injection molded articles due to additional orientation effects of the polymer in the direction of the flow. Crystallinity differences and crystallization rate are also impacted by the injection molding process such as the different cooling rates in the mold. Shrinkage of injection molded articles is a predictable phenomenon based upon the coefficient of shrinkage of a material and is inherent to the processes involving molded polymers. Some of the molding parameters that can affect shrinkage are injection pressure and hold times, mold temperature and part thickness (3).

Warpage is defined as the differential or anisotropical shrinkage of an injection molded part along the three different axes. This type of shrinkage leads to a part distortion, which can result in the reduction of mechanical properties as well as issues with fitting with other parts such as stackable boxes or crates and lids. Distortion is influenced by the polymer characteristics, the geometry of the molded article, the molding and cooling conditions, and additives such as pigments. The interaction of these various factors is complex and difficult to predict. These factors can usually be modified in order to obtain parts with substantially reduced warpage. Thicker areas of the part cool much slower than thinner parts and this different cooling rate influences the degree of crystallization and orientation of the spherulites. The thicker sections of the molded part can help reduce the amount of warpage by mechanically supporting the thinner areas.

The extent of warpage will very much depend on factors like molecular mass, degree of polymerization, amount of branching, and molecular weight distribution. The grade of polymer should not be changed when the warpage is highly important. Higher molecular weight polymers tend to be less prone to warpage than lower molecular weight ones. Branched polymers tend to warp less versus un-branched polymers.

Polyethylene is a semi crystalline polymer and its morphology is affected by the manner in which the polymer is crystallized. The crystalline regions have been studied extensively for many years (4-7) and polyethylene can be crystallized by a variety of processes that lead to the development of a complex crystalline morphology in molded products. Nucleation can be initiated by spontaneous, heterogeneous and orientation (or flow) induced nucleation. Heterogeneous nucleation, which involves the formation of crystal nuclei at the surface of some foreign particle or micro contaminant or a specifically added nucleating agent, is a primary mode of nucleation in polyolefins.

Types of pigments and additives play a key role for warpage. Small amounts of stabilizers or polymerization catalysts can act as nucleation agents and therefore influence the differential shrinkage. Fillers used in the formulation will also lead to warpage. Fillers such as the long glass fibers are responsible for the alignment of the polymer chains in the injection molding direction. The orientation of the polymer chains influences the orientation of the crystalline areas and is responsible for the difference in shrinkage along and perpendicular to the flow direction.

In comparison to polyethylene, polypropylene (PP) does not crystallize very quickly under normal conditions. Polypropylene does not present the same degree of warping challenges of molding high density polyethylene (HDPE) due to the latter's quicker crystallization kinetics.

Impact of Colorants

Colorants are an integral part of general industrial or consumer goods made of plastic components. Colorants are used for identification, creating a visual appeal, brand recognition, and for communicating hazards. Colorants can be broken down to two categories: pigments and dyes. Pigments, while imparting color, are insoluble in the matrix. Dyes on the other hand are soluble in the matrix providing transparency and brilliancy but have limitations in semi-crystalline polymers due to migration. Pigments can be further broken down into organic and inorganic pigments.

Inorganic pigments can be classified into standard metal oxides or complex inorganic colored pigments and effect pigments. Inorganic pigments provide durability and stability in extreme environments while offering some functional benefits such as Infrared (IR) reflectivity for creating cool surfaces. Effect pigments provide a variety of exciting and differentiating pearlescent and metallic finish to many plastic components especially in high end packaging applications.

Organic pigments are ubiquitous in the coloration of plastics. They are available in all color spaces consisting of multiple chemistries to be compatible in demanding plastic processing conditions. The selection of organic pigments will depend on the color space, polymer suitability, heat stability, fastness, food contact status, and strength. Organic pigments, however, have been found to play a critical role in the nucleation process of semi-crystalline polymers especially in polyolefins and contribute to dimensional instability of the injection molded parts. The distortion can also negatively impact the physical properties of the polymer. To address the significantly warping properties associated with the select organic pigments, surface treatments are applied to minimize or eliminate warpage issues. Therefore, the warping characteristics of an organic pigment will also need to be considered in the selection process especially when working with semi-crystalline polymers.

Inorganic pigments do not have a significant effect on the shrinkage of HDPE as they do not impact the crystallization rates like organic pigments. Organic pigments showed significant effects on increasing the rate of crystallization (8). There are some general differences between inorganic and organic pigments that might account for the differences that exist between these two general classes of colorants. Inorganic pigments tend to have more polar, and hydrophilic surfaces. Organic pigments tend to be more hydrophobic or lipophilic and have a more non-polar surface (9).

Electron microscopy has been used to study these differences between organic and inorganic pigments in HDPE (8). The combination of non-polar polyolefins with relatively non-polar organic pigments may promote interactions between the polymer and pigment surface that result in nucleation. The interaction between the organic pigment surface and the polymer matrix may change the material's normal crystallization kinetics. This may cause the morphology of the polymer to be different when compared to a system with no organic pigments. The nucleation effect imparted by the pigment creates different shrinkage rates and alterations in molded-in stresses that can result in dimensional stability problems. With inorganic pigments, there is minimal interaction with the polymer matrix because of relatively polar surface and its incompatibility with the polymer matrix.

There are a wide variety of organic and inorganic pigments with chemistries and surface modifications used in the plastics industry. Table 2 summarizes the major classes of organic and inorganic pigments used throughout the polyolefin industry. Pigments are typically classified by their color index number but they could have difference performance characteristics due to different preparation processes. Pigments with the same Colour Index (C.I.) number supplied from different manufacturers may not perform equivalently under the various processing conditions. Hence, the C.I. number is useful for general descriptions of the colorant chemistry, but not always for specific performance details.

The crystal habit of organic pigments can also influence the distortion behavior. Organic pigments have many different crystal shapes; some can be nearly perfectly hexagonal or cubic, but others can be highly acicular or needlelike. Even within a pigment generic classification, the chemical composition can have different crystal lattice arrangements. Alignment of needlelike or high length to diameter crystals of pigment may occur in flow fields; this may add to the distorting effect. Isotropic pigments appear to be less active in inducing warpage.

With the experience gained from both actual commercial use of pigments in distortion sensitive applications and specific testing by both production and laboratory evaluations, the impact of pigments on molded HDPE stability was tabulated. Pigments can be divided into three groups as shown in Table 3, depending on their influence on the shrinkage of HDPE injection molding systems. The pigments are classified as non-warping, low-warping or high-warping.

The classification of pigments into these categories enables the selection of pigments for distortion sensitive applications to be more rigorous. However, there are still many products and applications where the overall molding process permits the use of warping pigments as other factors override the effects of the pigment on the process. For the majority of applications, this is in fact the case and some of the colorants that are classified as warping are among the highest volume pigments used in the polyolefin industry.

The characterization of a pigment as high-warping does not prevent its use in polyethylene applications. Molding conditions and parameters can be optimized for a formulation containing pigments to minimize warpage. However, for a product that is to be molded in a variety of colors, it is preferable to not have different molding programs for each individual colorant system.

Test Methods for Warpage

In order to simulate the different molding conditions that one might find in the field, two different mold geometries were developed to evaluate the effect of pigments on shrinkage and warping. Disc and Plate tests are known methods that can determine the degree of shrinkage and warpage of a pigmented plastic article. For the plate test, a thin, elongated rectangular mold is devised to simulate linear flow through a mold or mold sections. The linear flow used in the plate test would introduce orientation effects on the polymer chains analogous to those found in molded bins or other rectangular containers. The disc test is designed to replicate radial flow in a center-gated disc shaped mold, analogous to the injection molding of circular lids and covers.

The plate test is based on the comparative measurement of actual shrinkage values of colored and uncolored rectangular plates after ageing in a hot water bath. The plates are produced by injection through a film gate covering the entire width of the test specimen, Figure 1. This ensures a parallel flow pattern and a development of orientation in the direction of flow.

The shrinkage is measured over the length of the plates (parallel to the direction of flow) and over the width of the plates (transverse to the flow lines), Figure 1. A total of ten plates each, colored and uncolored, are measured and the average values calculated. The shrinkage coefficients are expressed in ‰ as delta length (ΔL) and delta width (ΔW) relative to the dimensions of the mold. The warping tendency will increase with increasing difference between length and width shrinkage.

The disc test is based on the measurement of the actual distortion of colored injection molded discs after ageing in a hot water bath. The discs are produced by injection through a central gate, causing a swell flow, Figure 2. Orientation is primarily along the radial direction by shear flow and in the tangential direction by strain. If the shrinkage difference is negative (radial shrinkage is less than tangential shrinkage), the discs warp into a shallow bowl-like shape. In cases where the shrinkage difference is positive (radial shrinkage is greater than tangential shrinkage), the discs warp in a manner that yields a saddle like shape. The distortion is expressed in mm as delta height (ΔH) relative to the thickness of a non-warped disc, Figure 2. A measurement greater than 10 mm is classified as high-warping.

To prepare a test compound, a standard PE resin base is used to evaluate different pigments in a consistent manner. Pigments are typically evaluated at a fixed concentration such as 0.2% and are extruded in PE resin first prior to injection molding.

The injection molded test plates and discs are produced at 240°C into the mold that is tempered at 20°C. The mold dimension for the plate test is 174x49x2.5mm, with a film gate covering the entire width of the plate. The mold dimension for the disc test is 120x2mm. The molded plates or discs are placed in a water bath for 30 minutes at 90°C and then dried at room temperature overnight before measurements are taken.

The plate test is based on the comparison of shrinkage of pigmented and natural polymer and the results are represented graphically. The degree of distortion is measured in the disc test and any disc with a distortion greater than 10 mm is classified as high-warping.

In order to establish baseline molding conditions the base polymer is molded along with a high warping pigment control, Pigment Red (P.R.) 166, at the pre-established injection molding conditions so that each series can be related to a consistent set of controls. Figure 3 and Figure 4 are graphical representations of the quantitative measurements taken for these two control samples in addition to Pigment Yellow (P.Y. 93), subsequent to injection disk and plate samples. In the disk test, P.Y. 93 shows no significant impact on the dimensional stability of the molded article and the molded disk remains flat after temperature aging. An example of a warped disc with red pigments is shown in Figure 5. In the plate test, while there are small differences in the length and width measurements, these changes are not sufficient to cause any significant degree of distortion. P.R. 166 exhibits significant deviations from the base HDPE resin shrinkage values which results in significant distortion of the plastic moldings from each of the two mold geometries.

Pigments that are non-warping and low-warping in the plate and disc tests have been tested on actual production machines for bottle crates and boxes/lids. This confirms their suitability for actual applications. As polymers and processing conditions vary considerably from customer to customer and from one mold to the next, actual performance might vary due to subtle differences in the process. However, given the significant differences that are observed between high and low or non-warping pigments, knowledge of the general distortion tendencies of organic pigments certainly helps formulators select those with the best possible potential, while avoiding those which have the greatest tendency to contribute to dimensional stability problems. The screening procedure is performed with a strict set of molding parameters in order to generate a consistent basis for comparing the performance of commercial as well as experimental and developmental products. While the conditions are not universally representative of the molding conditions encountered in the field, as a screening technique the methodology works well in practice and has been used with a great degree of success for some time. A large number of both commercial and developmental products have been characterized by this method.

Recommendations to Address Warping

The root cause of distortion in molded plastics is the result of the combination of materials which includes the polymer, colorants, process stabilizers, fillers, molding conditions and mold design.

In order to minimize distortion, the mold designer has the capability of performing mold filling and structural analyses to adjust certain mold attributes to improve dimensional stability, the molder can adjust molding parameters to reduce distortion tendencies, and colorant suppliers can select from a finite pallet of colorants that are less likely to affect shrinkage values and have an impact on dimensional stability. For those applications which have the greatest tendency to distort and cause problems (for example, lids, closures, containers, etc.), non-warping or low-warping pigments can be specified. A list of low- and non-warping solutions available at different color spaces are shown in Table 4.

However, formulating with this reduced color palette does not always provide a total solution devoid of failures. Warping and distortion are complex phenomena. The molders need to better understand the fundamental causes of distortion and the differences not only between different polymer chemistries, but also within the same family as a consequence of polymer architecture. There are multiple factors that can be considered such as mold, process stabilizers, and the selection for the right colorant.

For the design and development of the mold, CAD programs are used to design molds with a broader processing profile that are more resistant to distortion. For the mold machine qualification and setup, evaluation of different materials (resin grades, colorants and suppliers) are needed to better understand which molding variables are the keys to troubleshooting distortion and setting parameters that are in the middle of a processing range, rather than just inside the acceptable range so that the molding cycle program is more robust.

When formulating with the colorants, the presence of a process stabilizer can impact the distortion characteristics as well. Non-warping pigments can be adversely affected by some additives to yield warping systems. Some additives such as high molecular weight hindered amine light stabilizers or a montanic ester may be beneficial when working with high warping pigment systems.

Innovation has led to the change in warping characteristics of a pigment. Application of a surface treatment or incorporating an additive have produced tailored organic pigments with reduced warping behavior. Diketo-pyrrolo-pyrrole based P.R. 254 is a good example of the pigment industry’s response to develop a low or non-warping pigment and enhance the value. A pigment was developed for reduced (low) shrinkage and warping with surface treatment technology. This pigment is especially useful for large moldings such as HDPE crates and containers. Yet another development for a high strength P.R.254 pigment provided the formulator with a nearly shrinkage-free and warp-free mid-shade organic red pigment. This is shown in Figure 6. Similar type of approach has been applied to Pigment Blue (P.B.) 15:1, 15:3 and P.Y. 110, to generate low or non-warping grades.

In the case of the colorants for distortion sensitive and critical applications, the selection of materials needs close attention at both the color matching and sampling stages. In order to identify and flag specific concerns and needs, improved communication between molders and colorant suppliers are needed to avoid formulations that can lead to severe distortions.

Conclusion

Distortion of warpage is a complex phenomenon. The differential shrinkage that is somewhat predictable in an unpigmented systems behaves very differently with the addition of colorants, fillers and process stabilizers. With some additional knowledge as to the root causes and major variables that can affect distortion, the application of the expertise that most molders have in-house and with the assistance of suppliers, it is likely that distortion problems can be minimized.

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Polymer	***% Shrinkage***
ABS	0.3-0.8
PC	0.5-0.7
PS	0.4-0.7
PP	0.8-2.5
HDPE	1.5-4.0
PA 6	0.5-1.5
PA 66	0.8-1.5
Acetal	2.0-2.5

Table 1. Shrinkage of various injected molded polymers

Hue	***Inorganic Colorants and Color Index***		***Organic Colorants and Color Index***	
Red	Iron Oxides	P.R. 101	Quinacridone	P.V. 19
			DPP	P.R. 254, 264, & 272
			Naphthol	P.R. 170
			Perylene	P.R. 149
Orange	Tin-Zinc-Titanate	P.O. 82	Azo	P.O. 79
			Benzimidazolone	P.O. 64
			DPP	P.O. 71 & 74
Yellow	Nickel Titanate	P.Y. 53	Isoindolinone	P.Y. 109 & 110
	Bismuth Vanadate	P.Y. 184	Disazo	P.Y. 93, 95, & 155
			Azo	P.Y. 62, 168, 191:1 & 229
			Benzimidazolone	P.Y. 180 & 181
			Pteridine	P.Y. 215
			Quinoaphtalone	P.Y. 138
Green and Blue	Ultramarine	P.B. 29	Phthalocyanine	P.B. 15:1 & 15:3
	Cobalt Aluminate	P.B. 28 &36	Phthalocyanine	P.G. 7 & 36
		P.G. 50	Indanthrone	P.B. 60
	Chromium Oxide	P.G. 17		
Violet	Manganese	P.V. 16	Quinacridone	P.V. 19
	Ultramarine	P.V. 17	Carbazole	P.V. 23 & 37
			Perylene	P.V. 29
Brown	Manganese-Antimony Titanate	P.Y. 164	Azo	P.Br. 23
	Iron-Chromium Oxide	P.Br. 29		
	Zinc Ferrite	P.Y. 119		
Black	Iron-Chromium Oxide	P.Br. 29	Perylene	-
	Cobalt-Chromium-Iron-Manganese Oxide	P. Bl. 27		

Table 2. Organic and inorganic pigments suitable in polyolefins

Classification	***Description of Warping Behavior***
Non-warping	No significant influence, either in lab tests or in practice.
Low-warping	Slight influence, as detected in lab test, but has been successfully used in practice.
Warping	Significant influence, both in lab tests and in practice, and not recommended for this application or only in combination with specific, warpage reducing additives

Table 3. Warping classification of pigments

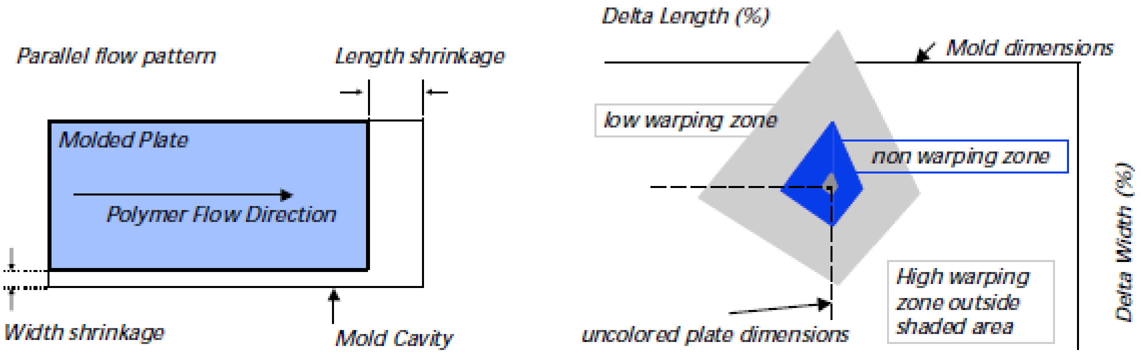

Figure 1. Warpage determination from a plate test and classification

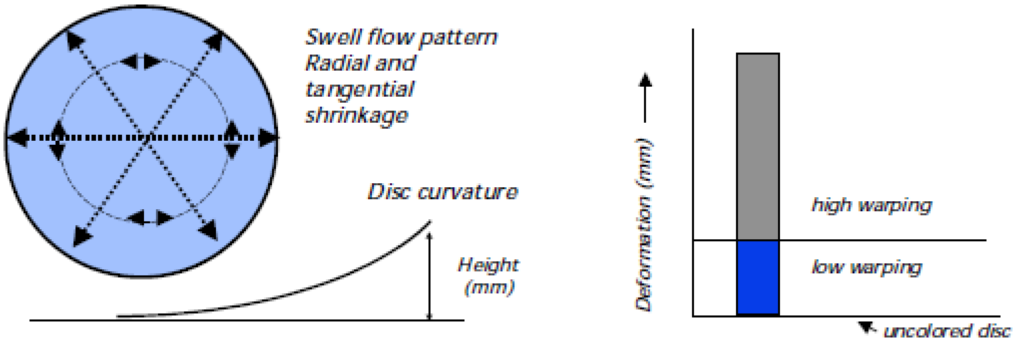

Figure 2. Warping determination from a disc test and classification

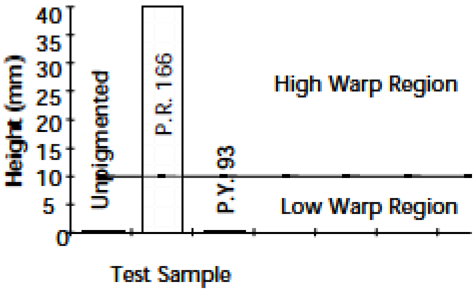

Figure 3. Disc test for P.R. 166 and P.Y. 93

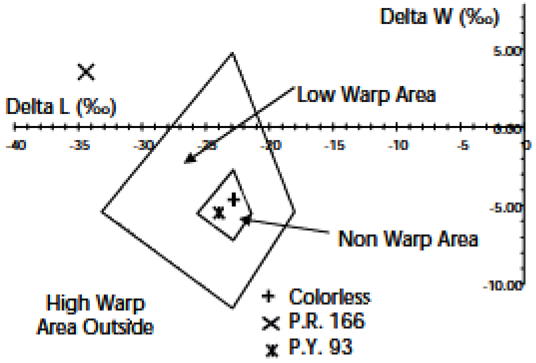

Figure 4. Plate test for P.R. 166 and P.Y. 93

Figure 5. Example of a warped disc with a red pigment

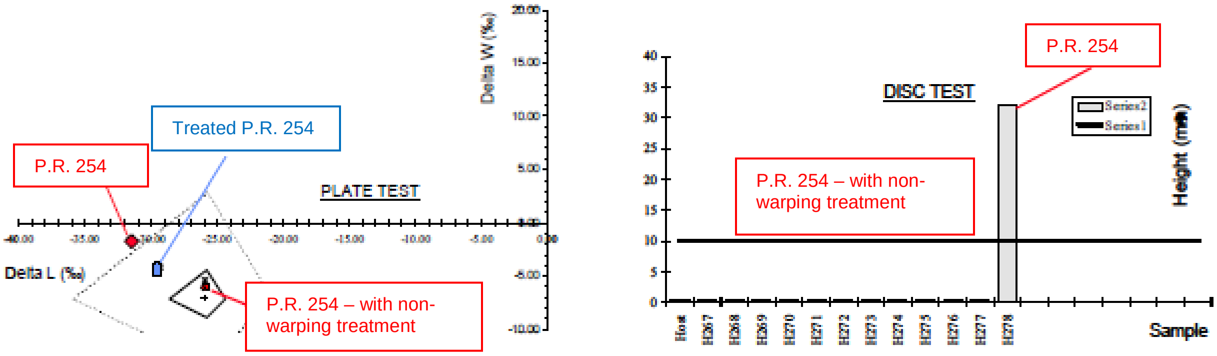

Figure 6. Plate and disc tests for P.R. 254 as is, low-warping and non-warping treatment

C.I.	Chemistry	Warping
P.Y. 128	Diszao condensation	None
P.Y. 168	Monoazo salt	None
P.Y. 93	Diszao condensation	None
P.Y. 95	Diszao condensation	None
P.Y. 220	Monoazo	None
P.Y. 191:1	Monoazo salt	None
P.Y. 138	Quinophthalone	Low
P.Y. 155	Diszao condensation	Low
P.Y. 215	Pteridine	Low
P.Y. 180	Benzimidazolone	Low
P.Y. 62	Monoazo salt	Low
P.Y. 183	Monoazo salt	Low
P.Y. 139	Isoindoline	Low
P.Y. 110 with additive	Isoindolinone	Low
P.O. 71	DPP	Low
P.O. 79	Azo salt	Low
P.O. 64	Benzimidazolone	Low
P.R. 220	Diszao condensation	None
P.R. 254 with additive	DPP	None
P.R. 264	DPP	None
P.R. 177	Anthraquinone	None
P.R. 48:2	Bona (Ca)	Low
P.R. 57:1	Bona (Ca)	Low
P.R. 57:1	Bona (Ca)	Low
P.R. 122	Quinacridone	Low
P.R. 202	Quinacridone	Low
P.R. 272	DPP	Low
P.R. 48:3	BONA (Sr)	Low
P.V. 19	Quinacridone	Low
P.V. 37	Dioxazine	Low
P.V. 23	Dioxazine	Low
P.B. 15:1 with additive	Cu-phthalocyanine	None
P.B. 15:4 with additive	Cu-phthalocyanine	Low
P.G. 7	Cu-phthalocyanine	Low

Table 4. Non-warping and low-warping organic pigments classified using the plate test

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