BENEFITS OF HIGH-PERFORMANCE ULTRAFINE POLYAMIDE POWDERS IN UV FORMULATIONS

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Abstract

This paper will deal with ultra-fine polyamide powders, which are polymers and copolymers of laurylactame and/or caprolactame obtained by direct polymerization. Those powders are micro-porous spherical beads with a very narrow particle size distribution. Those powders contrast from waxes due to their higher melting point, better chemical resistance and different migration process. We will address the benefits from using Polyamide powders in UV curing systems as it do not impact the viscosity of the UV/EB formulations even at a high level of addition. We will explain how it provides flexibility to the formulators providing low gloss, soft feel and textured coating without damaging the applicability and even improving the abrasion, scratch and anti-blocking performances.

Introduction

Ultra-fine polyamide powders are made by direct polymerization of laurylactame and/or caprolactame. Due to this unique process, the ultra-fine polyamide powders are virtually spherical, and have a micro porous structure and a very narrow particle size distribution. The grades are differentiated on polyamide type (PA 6, PA 12, PA 6/12), particle size (5 to 60 µm), melting point, and specific surface area. The density varies between 1.03 and 1.15. The ultra-fine polyamide powders are currently used as additives in water based, solvent based and 100% UV formulations such as paints, inks, wood coatings, automotive and industrial coatings.

Ultra-fine polyamide powders can be used to obtain low gloss UV top-coatings without increasing the viscosity or impacting the clarity of the systems. Besides the mechanical properties such as scratch resistance or abrasion resistance of the UV cured coating are improved. Thus, it is possible to make some high abrasion resistant low gloss UV coatings that can be used in different application including flooring, wood and plastic coatings. It has been also observed that ultra-fine polyamide powders lower the coating coefficient of friction providing anti-blocking and soft feel effect.

To illustrate this, gloss, viscosity, abrasion resistance and slippery property have been compared for formulations made with ultra-fine polyamide powders or silica additives. Both epoxy acrylate and urethane acrylate UV curable formulations have been studied, and applied on paper, wood, or plastic supports

Low gloss UV curable systems

Matting of 100% UV curable formulations is more difficult than solvent or water based conventional liquid coatings because there is no film shrinkage during the curing. When low gloss UV cured coatings are needed, some matting agents can be added to the formulation as long as the viscosity of the system is workable. Viscosity and gloss evolution results are based on the formulation below (Table 1). The different matting agents tested are listed in the Table 2.

Formulations		
Component	**Nature**	**Weight (grams)**
CN 104 A80	Epoxy Acrylate	101.25
SR 306	Tripropylene glycol diacrylate	78.75
Matting agent	Ultra-fine Polyamide Powders or Silica	20
Darocur 1173	Hydroxy-2-methyl-1-phenyl-propan-1-one	2

Table 1

Additive *Grades*	**Nature**	**APS (µm)**	**Surface Area (m^2/g)**	**Specific gravity**	**Oil Adsorption (g/100g)**
2001 EXD	Polyamide 12	10	4	1.03	0.77
3501 EXD	Copolyamide 6/12	10	20	1.07	1.7
3502 D	Copolyamide 6/12	20		1.07	
3202 D	Copolyamide 6/12	20		1.09	
1002 D	Polyamide 6	20		1.15	
2002 D	Polyamide 12	20		1.03	
2002 ES 3	Polyamide 12	30		1.03	
Lo-Vel HSF	high performance precipitated amorphous synthetic silica	10		2	170

Table 2

Viscosity evolution

The effect of the addition of different ultra-fine polyamide powders grades on the liquid system viscosity was compared to the effect of addition of silica. At a 10% weight level of matting agent, the viscosity of the formulation containing 3501 EXD is equivalent to the viscosity of the formulation containing silica, where as 2001 EXD exhibits a viscosity 25 % lower than the formulation containing silica. At a 15% weight level of matting agent, the formulation containing 2001 EXD has a viscosity 50% lower than the silica one. The addition of silica matting agents generates an increase of the viscosity; where as the addition of Polyamide 12 does not change the viscosity of the system (Figure 1).

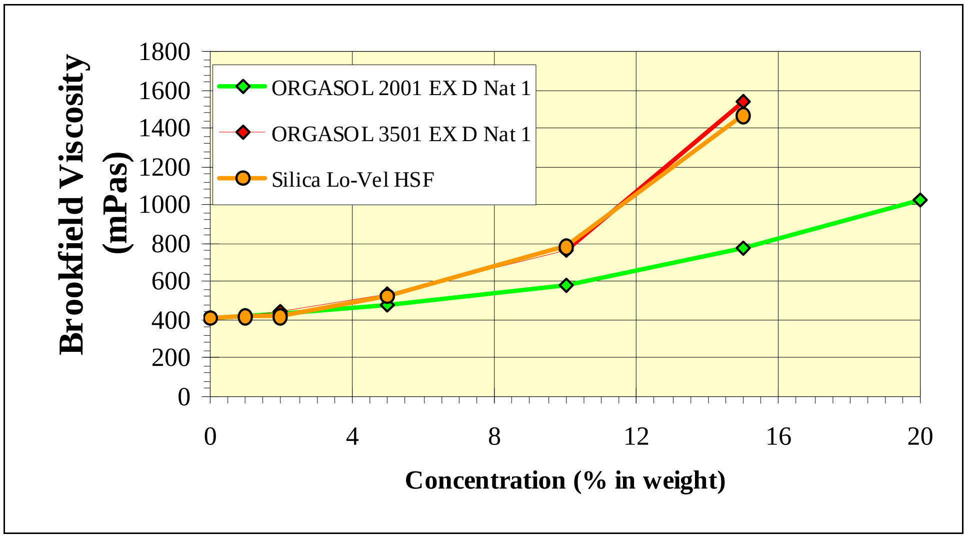

Figure 1: Viscosity versus Matting agents concentration

To better analyze the influence of the different ultrafine polyamide powder grades on the viscosity formulation, we have taken into consideration several parameters such as the nature of the polyamide, the average particle size of the ultrafine polyamide powders as well as the surface specific area.

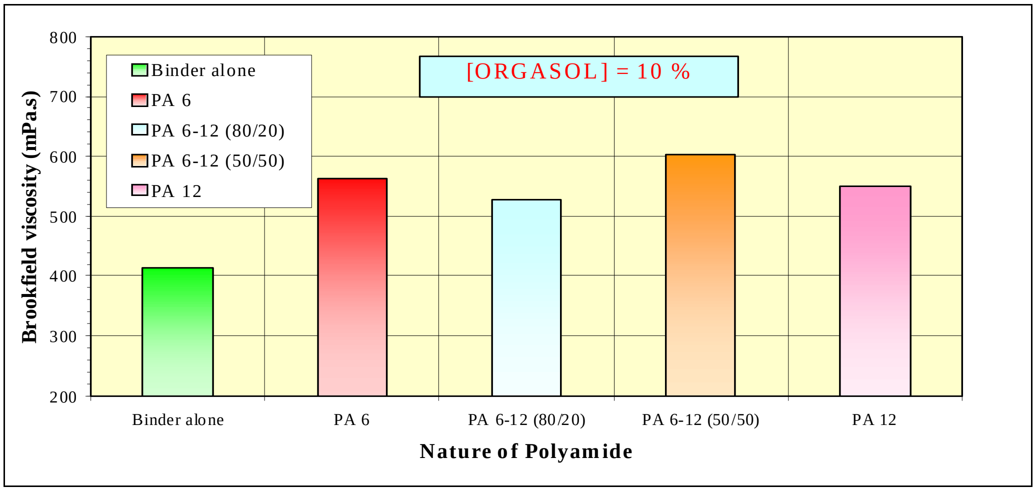

Figure 2: Viscosity versus Polyamide Nature

It seems that there are no significant viscosity differences with the 4 polyamide natures (Figure 2). Thus, we will focus on average particle size and the surface specific area of the ultrafine polyamide powders grades.

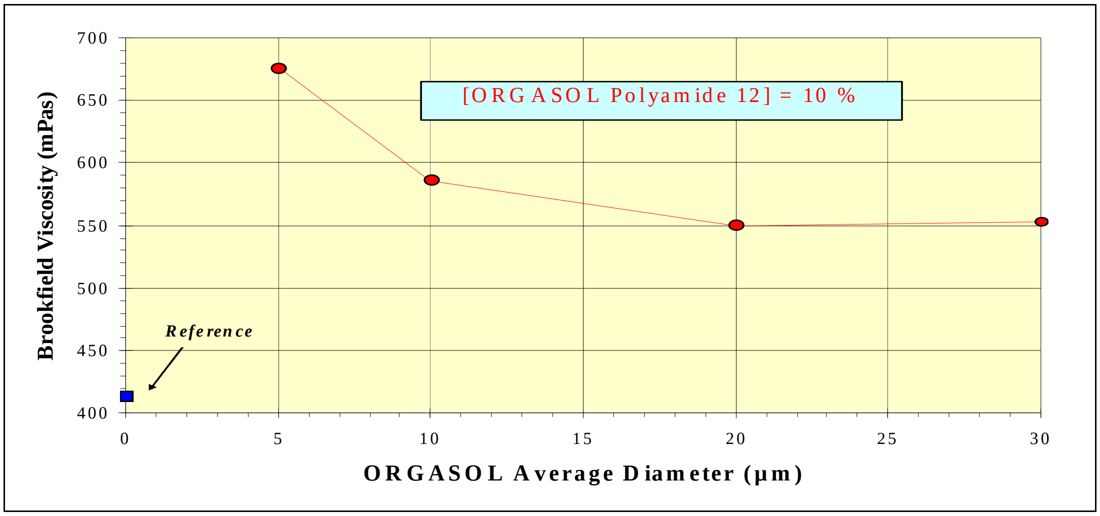

Figure 3: Viscosity versus Average Particle Size

For a given polyamide type and a given percent weight of in the formulation, the viscosity decreases when the average particle size increases. This is due to the fact that the concentration in volume as well as the number of particles per weight unit decreases when the average particle size increases. (Figure 3)

The other parameter to take into consideration is the Surface Specific Area of the ultrafine polyamide powders

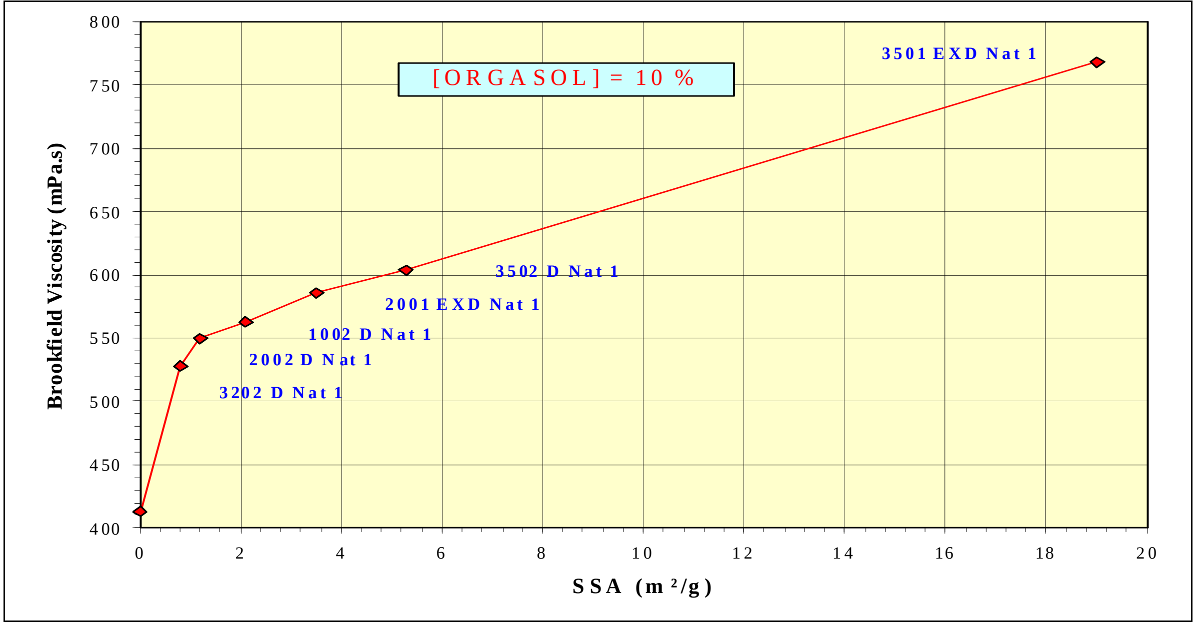

Figure 4: Viscosity versus Surface Specific Area

Ultrafine polyamide powders exhibit a micro porous physical shape which can vary with the polymerization parameters and the average particle size of each grade. The Figure 4 shows that the liquid system viscosity is related to the surface specific area of the polyamide powder.

Gloss evolution

It has been demonstrated that the optimum matting efficiency of a UV curable coating can only be achieved when there is a close match between the film dry thickness and the polyamide powders average particle size[1]. The very narrow particle size distribution of the polyamide powders enables such a close correlation

The other key parameter is the Surface Specific Area of ultrafine polyamide powders grade at a given particle size. We see on figure 6 that for a 12 microns thickness coating, 3501 EXD has a higher the matting efficiency than 2001 EXD due too its higher specific surface area.

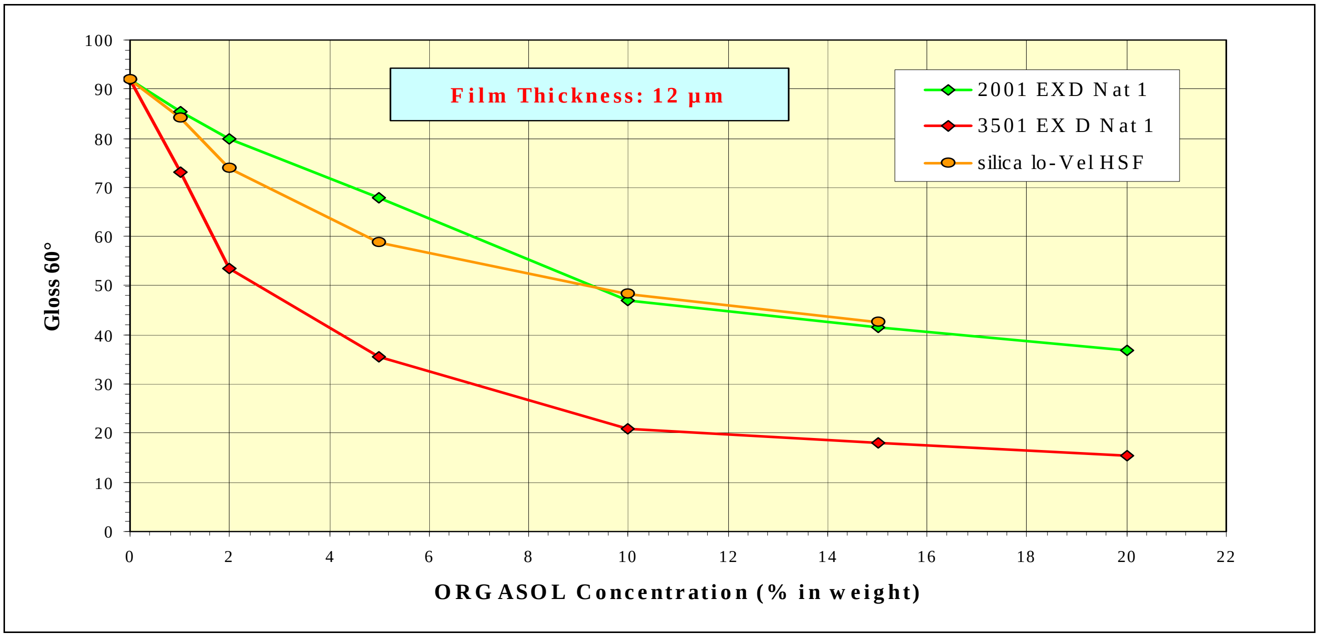

Figure 5: Gloss versus ORGASOL concentration

Examples of formulations

According to the previous results, two sets of formulation have been tested (Table 3): the first one is based on urethane acrylate (CN 947 Bn70), the second on epoxy acrylate (CN 104 A80).

Formulations	Nature	A	B	Formulations	Nature	C	D	E
CN 947 B70	Urethane acrylate	45,9	45,9	CN 104 A80	Epoxy acrylate	101,25	101,25	101,25
SR 238	1,6 Hexanediol diacrylate	33,7	33,7	SR 306	Tripropylene glycol diacrylate	78,75	78,75	78,75
SR 454	Ethoxylated (3) trimethylolpropane triacrylate	6	6	2001 EXD	Polyamide 12 Particle size = 10 microns	20	/	/
2001 EXD	Polyamide 12 Particle size = 10 microns	7	/	3501 EXD	6/12 copolyamide Particle size = 10 microns	/	20	/
Silica 1	High porous untreated amorphous silica. Particle size = 5 microns	/	7	Silica 2	High porous untreated amorphous silica. Particle size = 10 microns	/	/	20
TF1780	PTFE/PE wax	1	1	Darocur 1173	Hydroxy-2-methyl-1 -phenyl-propan-1-one	9	9	9
CN 385	Benzophenone	5	5					
Irgacure 184	Photoinitiator	1	1					
Fluorad FC 430	Fluorosusrfactant	0,2	0,2					
Perenol E1	Silicone-free defoamer	0,2	0,2					
Viscosity								
RVT Brookfield visc. (n°3 spindle - 50 rpm)		365 mPa.s	1050 mPa.s	RVT Brookfield visc. (n°3 spindle - 100 rpm)		585 mPa.s	770 mPa.s	790 mPa.s
Application & Curing								
Thickness (µm)		12		Thickness (µm)		12		
UV light (W/cm)		120		UV light (W/cm)		120		
Line speed (m / mn)		8		Line speed (m / mn)		16		
Gloss								
Gloss 60°- Wood		15	15	Gloss 60°- Paper		44	21	48
Gloss 60°- PVC		32	28					

Table 3: Viscosity and Gloss - Influence of the matting agent

In the formulations A and B (urethane-acrylate / 7 % of matting agent), the system containing ultrafine polyamide powders has a viscosity 3 times lower than the one with the silica when achieving the same 60° gloss.

In the formulations C, D and E (epoxy-acrylate / 10 % of matting agent), the viscosity of the formulation containing 3501 EXD is equivalent to the viscosity of the silica formulation, but the 60° gloss is twice lower than the gloss obtained with the silica formulation. The formulation containing 2001 EXD exhibits a viscosity 25 % lower than the formulation containing silica for a the same matting efficiency.

As a conclusion, in those two formulations, ultrafine polyamide powders exhibit equivalent or better matting efficiency and minimal impact on the viscosity of the system as shown in Figure 7. The fact that the matting efficiency is linked to the particle size / film dry thickness ratio enables to adjust the choice of the polyamide powder grade to the coating thickness.

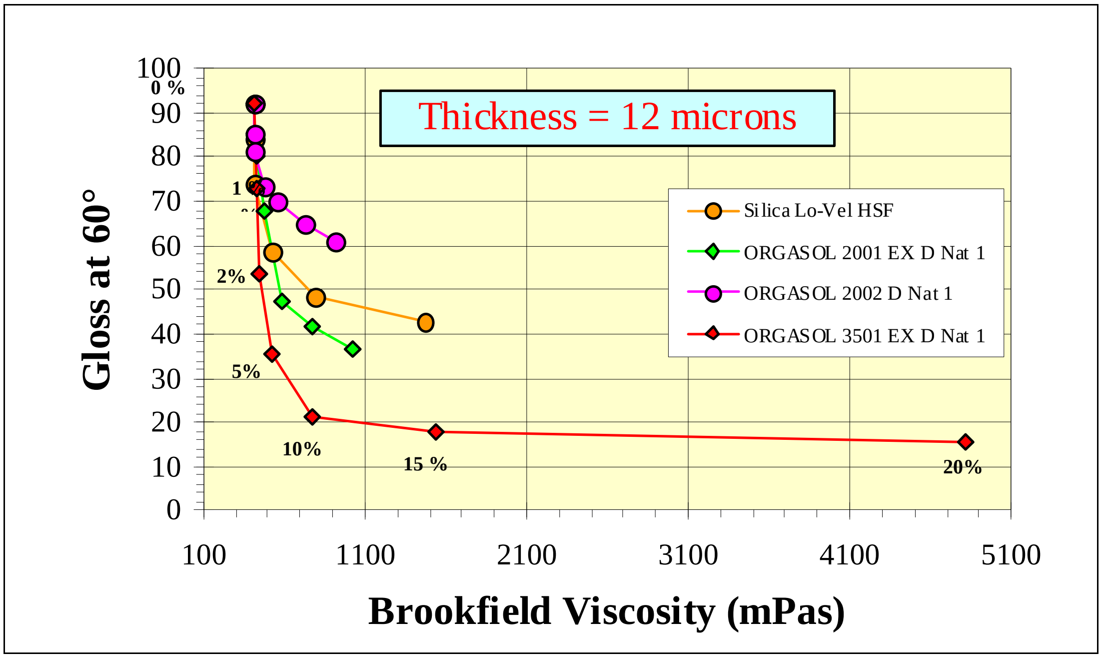

Figure 6: Gloss versus Viscosity

Impact of ultrafine polyamide powders on UV curable coating performance

Abrasion resistance can be achieved by selecting the right resin system[2]. Low gloss 100% UV coating requires the use of significant loading matting agents. Nevertheless, the use of matting agent like silica may cause several problems. They tend to increase the viscosity of the system, decrease the abrasion resistance, induce burnishing and create haziness on the final UV cured coating. The addition of ultrafine polyamide powders, as shown later in this paper, improves the abrasion resistance of the UV coating preventing any burnishing, while maintaining a low viscosity. Also, with a refraction index of 1.53 comparable to most of the resin, ultrafine polyamide powders do not impact the clarity of the coating. A previous study[3] demonstrated that the polyamide powders can also provide a slipping resistance 30 % lower than silica at same loading.

Table 3 reports abrasion resistance testing performed on the epoxy-acrylate system. Viscosity measurements confirm the non thixotropic behavior of the polyamide 12 powders. The abrasion resistance has been performed under ASTM D 4060 (Taber - CS 17 wheel - 1Kg load). To determine the abrasion resistance, we recorded the weight loss after each 100 rotations, up to a total of 1000 rotations. A small loading of ultrafine polyamide powders allow to achieve optimum abrasion resistance abrasion. In the UV curable system tested, the optimum level is between 1 and 4% by weight. This level enables to improve the abrasion by more than 25 %.

Formulations		F	G	H	I
CN 104 A80	Epoxy acrylate	112,5	111,37	110,25	106,87
SR 306	Tripropylene glycol diacrylate	87,5	86,63	85,75	83,13
2001 EXD	Polyamide 12 Particle size = 10 microns	/	1	4	10
Darocur 1173	Hydroxy-2-methyl-1 -phenyl-propan-1-one	10	9,9	9,8	9,5
Viscosity					
RVT Brookfield viscosity (n°3 spindle - 100 rpm)		413 mPa.s	420 mPa.s	422 mPa.s	472 mPa.s
Application & Curing					
Thickness (µm)		100			
UV light (W/cm)		120			
Line speed (m / mn)		16			
Abrasion resistance					
Weight loss after a 1000 cycles (mg)		93,5	91,6	75	77

Table 4: Abrasion Resistance - ORGASOL ® powders

CONCLUSIONS

Ultrafine polyamide powders are efficient matting agents for UV cured system. The optimization of the ratio between the coating dry thickness and the average particle size is critical to achieve maximum efficiency. Polyamide 12 powders have no impact on the viscosity on the UV system contrary to silica. The matting efficiency and the impact on viscosity depend mainly on the particle size and specific surface area of the polyamide powder.

By using ultrafine polyamide powders, a high level of abrasion protection can be achieved avoiding the burnishing typically caused by silica. Also, the addition of ultrafine polyamide powders does not modify the clarity of the system, while decreasing the slipping resistance of the coating.

All the advantages provided by the ultrafine polyamide powders are highly beneficial for applications such as flooring, plastic and wood coating.

REFERENCES

[1] M. Bernard, E. Valot "Matting of UV Curable Formulations with Polyamide Powders" Radtech 1995, Maastricht.
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[3] P. Leroy, K. Loyen, K. Zahouily, M. Bernard, “Abrasion resistant uv-cured coatings influence of various matting agents” Radtech 2001, Basel