Fine Grinding of Carbon Black

Harry Way
Netzsch Incorporated, Exton, Pennsylvania

Steven A. Schwartz, Sallie J. Lee and Adam Chan
Lyondell Chemical Company, Newtown Square, Pennsylvania

Abstract

Producing fine particle size and narrow particle size distributions in aqueous organic pigment dispersions is a significant challenge. Therefore, optimum utilization of both bead milling and chemical technologies is necessary to most efficiently achieve stable dispersions with the target particle size characteristics. This paper describes the effects of bead mill size and dispersant chemistry on particle size reduction for difficult-to-disperse carbon black pigment.

Introduction

Dispersion of carbon black pigment in water via bead milling is very difficult due to the extremely fine particle size of this material. Long exposure times are often required to achieve the desired degree of dispersion. This can lead to wear on the grinding media that reduces milling effectiveness due to both bead size irregularities and contamination. Moreover, long exposure times increase the natural tendency of pigment particles to agglomerate during the milling process, and this leads to the production of unstable dispersions. The goal of the test work done for this discussion was to show that carbon black disperses to an extremely fine particle size very quickly through judicious choices of grinding media size and dispersant copolymer.

Dispersion techniques typically include a media milling/grinding process in which the pigment agglomerates are broken down into smaller agglomerates and/or individual particles which are wetted by the carrier medium. We must consider the tremendous amount of surface area of finely divided carbon black pigment particles. The dispersion vehicle must displace contaminants such as air from these surfaces and wet the pigment particles. Pigment dispersants are provided in the pigment dispersion to facilitate the wetting process. In addition, they are important to the suspension and homogeneous dispersion of the pigment particles in the carrier medium as they are being milled and subsequently during storage. The function of the pigment dispersant is to therefore wet, disperse, and stabilize the pigment dispersion in its carrier solvent and to maintain stable particle distributions in the finished letdown formulation.

Typical high-speed dispersing with a sawtooth blade rotating at a shear rate of 600-800 sec^{-1} begins to de-agglomerate pigment particles. But for fine grinding of carbon black, high-speed dispersion does not completely de-agglomerate the particles. This is the purpose of the bead mill. The bead mill works like a filtering system. A spinning rotor activates the beads. The collisions and compacting between the beads break the particles apart. The mixing action of the machine over time results in a stable dispersion.

One of the fundamental principles of the bead mill has always been the grinding media size and to a certain extent its density. However some importance must be placed on the charge level of the beads as we can see from Figure 1. Figure 1 shows that decreasing the bead size and increasing the bead charge results in tighter spacing between the beads. This is the underlying principle that allows bead mills to produce fine particle size dispersions. The mill works like a large filtering mechanism, and the beads control the particle size of the dispersion produced by the mill.

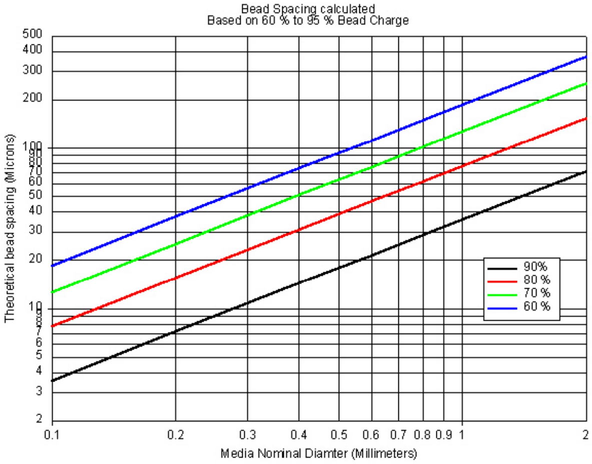

Figure 1. Bead Spacing Based on 60 to 95% Bead Charge

Therefore to quickly produce a fine particle size dispersion, very fine media should be used. However to produce a fine particle size dispersion quickly the chemistry must be optimized to produce a stable dispersion. Also the slurry introduced into the mill must be properly prepared to allow this rapid fine grinding to occur without problems such as foam or a large amount of entrained air to impede the dispersion process.

Lyondell Chemical Company supplied several different dispersant copolymers for this work. They are described as water-soluble acrylic/polyether comb-branched copolymers. Their basic structure represented in Figure 2. Both electrostatic and steric mechanisms contribute to the development of stabilized pigment dispersions. Electrostatic stabilization is dependent upon the formation of a repulsive charged double layer potential due to the acrylate "anchor" groups on the backbone of the comb-copolymer. Extending into the solvent from these anchor groups are pendant polyether macromonomers. Steric stabilization is related to configurational restrictions of these pendant chains as particle surfaces approach each other. Thermodynamically, the free energy of the system increases as the particles approach one another (increase in ΔG due to decrease in ΔS), which provides the energy of repulsion.

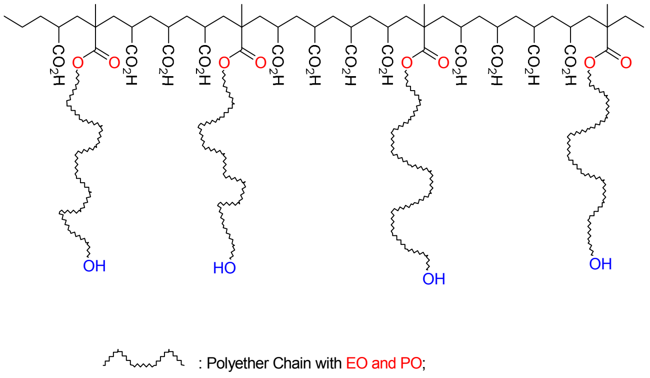

Figure 2. General Structure for Comb-Branched Copolymer

The copolymer as shown in Figure 2 is contains acrylic acid and polyether macromonomer units. Other ethylenically unsaturated comonomers and macromonomers may be incorporated into the structure. Other possible structural variations include the density of the polyether pendant group in the molecule and its solubility. This latter property is a result of the molecular weight and the level and type of alkoxylation. In addition, the molecular weight and polydispersity of the polyether/acrylic comb-branch copolymer is a controllable property. A high degree of structural flexibility for the copolymer allows for optimization as a function of the pigment type, the carrier medium, and the final application.

The objective of the work was to evaluate the effects of the different dispersant copolymer structures and grinding media size on particle size reduction and stability.

Results

The tests were made using a NETZSCH Labstar Laboratory grinding mill. We premixed NegroMex carbon black, a pigment typically used for rubber applications. This is a coarse carbon black that is difficult to grind to a fine particle size.

Table 1. Summary of Labstar Tests with Varying Bead Size

	Dispersant #2		Dispersant #4		Dispersant #10	
	0.5 mm Beads					
Mill Residence Time (Minutes)	Mean Particle Size (Microns)	99% of particle < (Microns)	Mean Particle Size (Microns)	99% of particle < (Microns)	Mean Particle Size (Microns)	99% of particle < (Microns)
0.0	3.483	13.184	0.344	1.165	3.204	18.895
0.6	0.471	1.759	0.358	1.597	0.617	5.094
5.7	0.409	1.047	0.338	1.262	0.203	0.553
	0.2 mm Beads					
0.0	3.483	13.184	0.344	1.165	3.204	18.895
0.6	0.303	1.021	0.249	0.911	0.252	0.822
5.7	25.235	80.944	0.208	0.687	0.142	0.358
	0.1 mm Beads					
0.0	3.483	13.184	0.344	1.165	3.204	18.895
0.6	1.377	14.830	0.233	0.686	0.268	0.876
5.7	21.049	68.308	0.221	0.804	0.136	0.296

Table 1 summarizes the results of the tests. We see that using smaller diameter beads results in a finer particle size as expected. Three different acrylic/polyether comb-branched copolymers were tested that spanned variations in molecular weight, polyether composition, and backbone comonomers. Dispersant #2 is the least effective dispersant, Dispersant #4 is moderate, and the Dispersant #10 is the most effective in terms of the ultimate particle size. It is interesting however, that Dispersant #10 was not the most efficient dispersant. This is probably due to the higher level of foam due to air entrained during preparation of the premix using the high-speed disperser. Future work is planned to evaluate the advantages of mechanical de-aeration of the slurry prior to bead milling.

Summary

1 – Selection of dispersant chemistry is critical to obtaining a stable dispersion. Tests must be run to determine the correct type of dispersant as well as the proper level, i.e. percent dispersant on pigment.

2 – Using smaller bead diameter results in finer grinding faster, reducing the exposure time of the slurry to the milling process

3 – Correct dispersant level and milling with small grinding media results in a very narrow particle size distribution. The problem of oversize particles may be due to poor dispersion chemistry in combination with larger beads not effectively grinding the oversize particles.