

EFFECT OF CARBON BLACK PHYSICAL FORM ON DISPERSION RATE

Presented by:

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ABSTRACT

The proper dispersion of carbon black in a coating system is critical in order to obtain consistent end-use properties such as color, gloss, and viscosity. The selection of the carbon black grade and whether the carbon black is in fluffy or pelleted form are important dispersion criteria. This paper evaluates the effect of the physical form of the carbon black upon dispersion. Novel carbon black dispersion techniques will be discussed.

This paper is based on a designed experiment which considered the differences in the physical form of carbon black (fluffy vs. pellet) and various grinding media (glass, zirconium silicate, and steel). The responses measured are dispersion, color, and gloss.

INTRODUCTION

The selection of a carbon black for use in paints and coatings presents processors with numerous options. Carbon black is available in two general physical forms: fluffy and pelleted. In addition, a variety of dispersion grinding media are available, including steel, zirconium silicate, and glass. Optimal dispersion of carbon black in a resin system is required for optimal performance properties such as color and gloss.

The research reported in this paper was designed to evaluate the dispersion and end-use performance of fluffy and pelleted carbon blacks in different grinding media. The results are presented to assist processors in the coatings market in choosing between pelleted and fluffy grades of carbon black and in selecting an appropriate grinding medium.

BACKGROUND

Carbon black is a particulate form of industrial carbon produced by thermal cracking or thermal decomposition of a hydrocarbon raw material. Carbon blacks are composed of spherical, semi-graphitic particles ranging in diameter from 10-100nm and in surface area from 25-1500 m²/g. These particles fuse together in clusters that form the characteristic units of carbon black called aggregates.

The majority of carbon black is produced using the oil furnace process, a highly efficient method that permits rigid control of morphological properties. Many different grades of carbon black are produced for use in coatings and other products. Grades of carbon black are primarily classified on the basis of two properties: surface area/particle size and structure.

Particle Size

The particle size of carbon black is a measurement of the diameter of the primary particle that makes up the primary aggregate of the black. This should not be confused with the size of the primary aggregate, which is related to carbon black structure. The particle size is measured either directly via electron microscopy or more commonly by indirect surface area measurement. Since surface area is expressed per unit weight, the higher the surface area, the smaller the particle size (assuming standard low-porosity blacks). The particle size affects the color (jetness and tinctorial strength), as well as the dispersibility of the carbon black. Smaller particle size carbon blacks are jetter and have higher tinctorial strength, but are also more difficult to disperse.

Structure

A carbon black whose primary aggregates are composed of many prime particles with considerable branching and chaining is referred to as a high-structure black. If the primary aggregates consist of relatively few prime particles forming a more compact unit, the carbon black is referred to as low-structure. Structure affects the loading (viscosity), gloss, and dispersibility of the carbon black. Low-structure blacks allow higher pigment loadings and impart higher gloss because of their lower vehicle demand. Low-structure blacks also incorporate (wet-out) better than high-structure blacks because they have less occluded air. However, because of the closer packing of aggregates, they are more difficult to disperse.

PHYSICAL FORM - DENSITY

The oil furnace process yields carbon black in a fluffy, extremely low-density powder form. In order to allow efficient handling, the density of the carbon black must be increased. The densification process involves removing occluded air by agitation, either dry or with the addition of water. When this agitation is rotational in nature, spherical pellets will be formed.

Carbon black may be used directly in its fluffy form or as pellets, which are denser. Pelleted carbon blacks are easier to handle and incorporate faster than fluffy carbon blacks; however, as this paper will show, pelleted blacks are more difficult to disperse. This is because the densifying process increases the proximity of the aggregates and thus increases the Van der Waals attractive forces which must be overcome in the dispersion process.

The dispersion of carbon black is critical to its performance in a coating. A carbon black is optimally dispersed when it has been separated into discrete primary aggregates. The dispersion process does not break down carbon black aggregates into primary particles. The basic unit of carbon black remains the primary aggregate, not the individual particle.

The dispersion process involves several steps. The incorporation stage, also known as wetting, removes occluded air and distributes the carbon black through the resin system. Dispersion (deagglomeration) can then occur to break down the carbon black agglomerates into smaller aggregates and ultimately into primary aggregates.

The amount of energy or work that is needed in the dispersion step for carbon black (or any pigment) is proportional to the forces holding the agglomerates together. Rumpf [1] has reported that the strength of an agglomerate is:

$$T = N_{agg} j B_z$$

T = Strength of an agglomerate

N_{agg} = Number of agglomerates per unit area

j = Number of contact points per aggregate

B_z = Attractive force per contact (component perpendicular to breakage plane)

Using this formula, Medalia has related the strength of the agglomerate to the surface area and Dibutyl Phthalate (DBP) oil absorption of the carbon black [2].

$$T = \frac{0.00147 (SA)^2 \exp \left(\frac{1.128}{DBP + 0.47} \right)}{(DBP + 0.47)^{3.86}} B$$

Thus, the agglomerate is expressed in terms of surface area and DBP absorption. From this, it is obvious that high-structure blacks are easier to disperse than low-structure blacks, and also that high-surface-area blacks are more difficult to disperse than low-surface-area blacks.

The physical form of the carbon black also affects the dispersibility of the carbon black. In many cases, even more than the morphological properties, pelleted carbon blacks are more difficult to disperse than fluffy blacks because of the significant increase in Van der Waals forces caused by the compaction that occurs during pelletization. This is confirmed by our experiments.

EXPERIMENTAL

Fluffy (MONARCH® grades) and pelleted (BLACK PEARLS® grades) carbon blacks (Table I) were evaluated for dispersion time using glass, zirconium silicate, and steel mill media (Table II).

Table I. Carbon Black Analytical Data

Grade	Nitrogen Surface Area (m ² /gm)	DBP Absorption (cc/100mg)	Density (lbs/ft ³)
BLACK PEARLS 120	25.6	67.6	32.7
MONARCH 120	26.4	69.2	14.5
BLACK PEARLS 280	37.2	116.3	21.5
MONARCH 280	37.6	132.5	6.4
BLACK PEARLS 570	105.5	114.4	21.7
MONARCH 570	102.2	110.9	12.8
BLACK PEARLS 900	274.2	59.5	31.2
MONARCH 900	246.6	70.9	13.1

Table II. Grinding Media

Media Type	Specific Gravity
Glass	2.55
Zirconium	3.85
Steel	7.2

The mill base was formulated as shown in Table III.

Table III. Mill Base Formulation

Alkyd Resin (Cellokyd 3378 HFN)	182.0 grams
Mineral Spirits	101.5
Dispersing Agent (Nuospense 657)	7.0
4% Calcium	7.0
Carbon Black @ 15% Loading	<u>52.5</u>
	350.0 grams

The pigment loading in the mill base formulation was adjusted to give a viscosity of 80-120 Krebs Units using a Brookfield Model Ku-1 Viscometer. The mill base formulation was mixed on a Dispermat for 30 minutes at 5,000 RPM. The mill base was then loaded into a Red Head L-2 vertical mill and dispersed to a 7 Hegman grind. The mill base was then reduced to 2.0% carbon black using the formula in Table IV. The reduced mill base was mixed using a Dyna-mix Lab Stirrer for 30 minutes.

Table IV. Reduction Formulation

Mill Base	13.3 grams
Alkyd Resin (Cellokyd 3378 HFN)	61.6
Drier (6% Cobalt NAp-ACL)	0.86
Drier (6% Zirconium HCX CEM)	1.7
Anti-skinning Agent (Exkin #2)	0.26
Mineral Spirits	<u>22.28</u>
	100.0 grams

DISPERSION EVALUATION

Hegman

There are many different techniques that can be utilized to measure dispersion quality [3]. Since the Hegman gauge is still widely accepted as the best technique for monitoring dispersion on the production floor, it was chosen as the technique for this paper.

Other Techniques

Dispersion was also evaluated by measuring the agglomerate size [4]. Digital imaging techniques have been developed which enable us to count and measure particles using optical microscopy. Cabot's laboratory configuration consists of a video camera mounted onto an optical microscope on which a glass slide of the final paint is placed. Visible light is then passed through the slide to measure particles over a two-dimensional detector that digitizes the particle structure and the area percentage of those particles. Dedicated software is used to extract the quantitative information. Figure 1 is typical of the decrease in agglomerate size during the dispersion process. This figure represents the percentage of agglomerates (minimum vs. maximum size) measured during the milling process for MONARCH 570 carbon black.

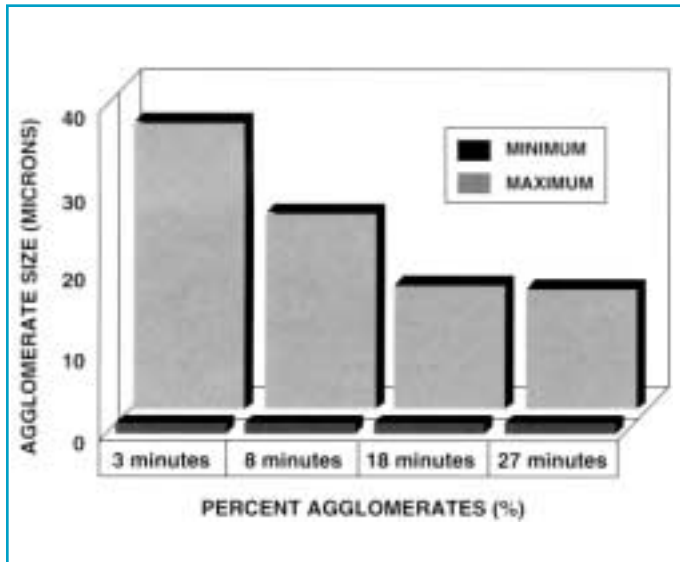


FIGURE 1.
Measurements of Aggregate Size and Quantity
for MONARCH 570 carbon black.

Dispersions were also evaluated using optical microscopy at 100X and 500X to assess the size distribution of undispersed agglomerates. The dispersions were rated using Cabot's dispersion classification system [5].

As shown in Figures 2 and 3, the size of the agglomerates decrease as the dispersion time increases and correlates reasonably well with the Hegman gauge rating for "poorer" dispersion. However, the microscope technique is more sensitive than the Hegman gauge at assessing the higher levels of dispersion, such as those needed for automotive topcoats.

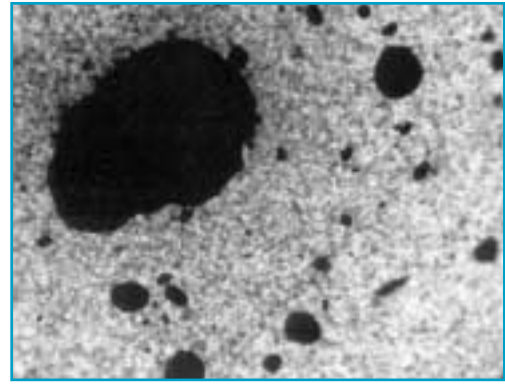


FIGURE 2.
Dispersion of MONARCH 570 carbon black
at 3 min. (500X).

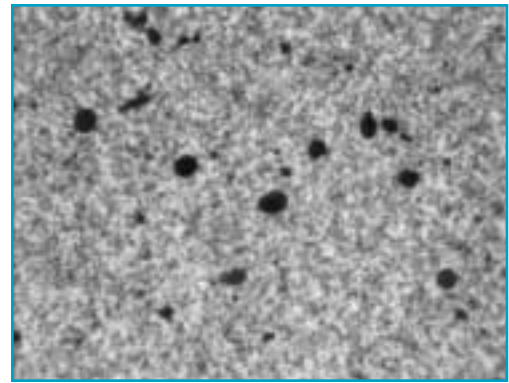


FIGURE 3.
Dispersion of MONARCH 570 carbon black
at 27 min. (500X).

EVALUATION OF DISPERSION RATE

Pairs of carbon blacks -- a fluffy grade (MONARCH) and a similar pelleted grade (BLACK PEARLS) -- were dispersed in a Red Head L-2 vertical mill. At three-minute intervals samples were removed and evaluated on the Hegman Grind scale. The time required to reach 7 Hegman, as well as the rate of dispersion, was determined for each sample and each grinding medium: glass, zirconium silicate, and steel.

RESULTS AND DISCUSSION

Time

Figures 4, 5, 6, and 7 show the time required to achieve a 7 Hegman grind for the four pairs of carbon black. These results indicate that for pairs of carbon black with equivalent surface area, the higher-structure blacks disperse faster than lower-structure blacks as illustrated by Figure 4 vs. Figure 5. When structure is equivalent, lower-surface-area blacks disperse faster (Figure 4 vs. Figure 7). The issue becomes more complex when there is a difference in both structure and surface area. When different blacks exhibit a large enough difference in surface area, the surface area becomes the dominant factor in ease of dispersion. The higher the surface area, the more difficult the dispersion. When two blacks have similar surface area, structure becomes more dominant when determining the ease of dispersion.

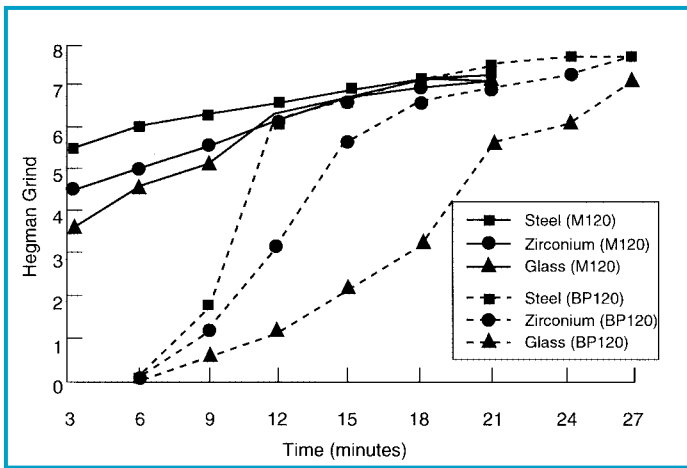


FIGURE 4.

Dispersion of MONARCH 120 and BLACK PEARLS 120 carbon blacks using steel, zirconium silicate, and glass media.

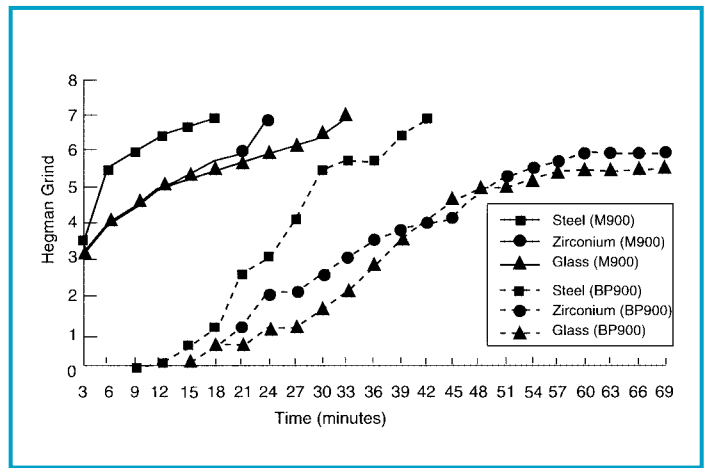


FIGURE 7.

Dispersion of MONARCH 900 and BLACK PEARLS 900 carbon blacks using steel, zirconium silicate, and glass media.

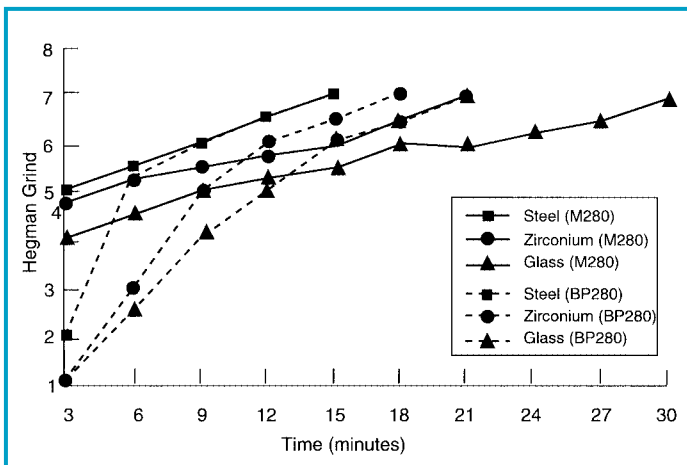


FIGURE 5.

Dispersion of MONARCH 280 AND BLACK PEARLS 280 carbon blacks using steel, zirconium silicate, and glass media.

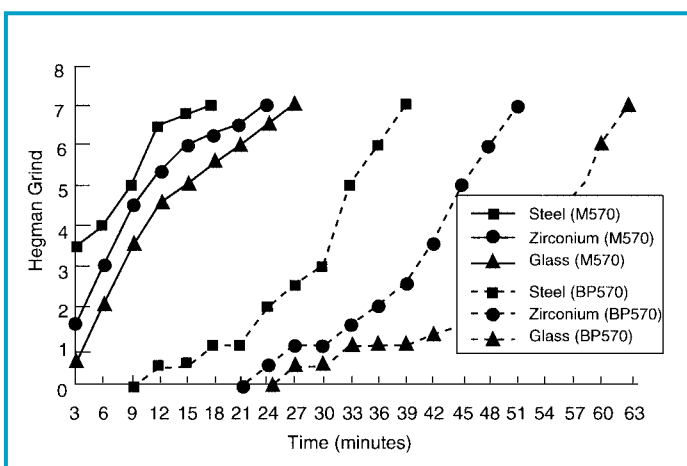


FIGURE 6.

Dispersion of MONARCH 570 and BLACK PEARLS 570 carbon blacks using steel, zirconium silicate, and glass media.

GRINDING MEDIA

The effect of the three grinding media (steel, zirconium silicate, and glass) on a typical fluffy and pelleted black is shown in Figure 6. In all samples evaluated, the higher the density of the medium, the more efficient (faster) the dispersion. This is because the higher density media impart more force upon each impact than does a lower density medium. It follows the laws of physics that the force of an impact is proportional to the mass of the moving object.

Physical Form

As expected, in all cases the fluffy carbon black dispersed faster than its pelleted counterpart as shown in Figures 4 - 7.

Performance (Color and Gloss)

The jetness and gloss of the final system are not affected by the physical form of the carbon black and the grinding media as long as the dispersion is equivalent. The jetness of MONARCH 900 carbon black vs. BLACK PEARLS 900 carbon black is independent of dispersion media as seen by the L* (lightness/darkness) values shown in Figure 8. Between the physical form there is a very slight improvement in jetness for fluffy as compared to pellets, which is explained by the slight improvement in microscopic dispersion achieved with fluffy blacks over pelleted blacks. A similar phenomenon is seen for MONARCH 570 carbon black vs. BLACK PEARLS 570 carbon black in Figure 9. There was virtually no difference in gloss (Figure 10).

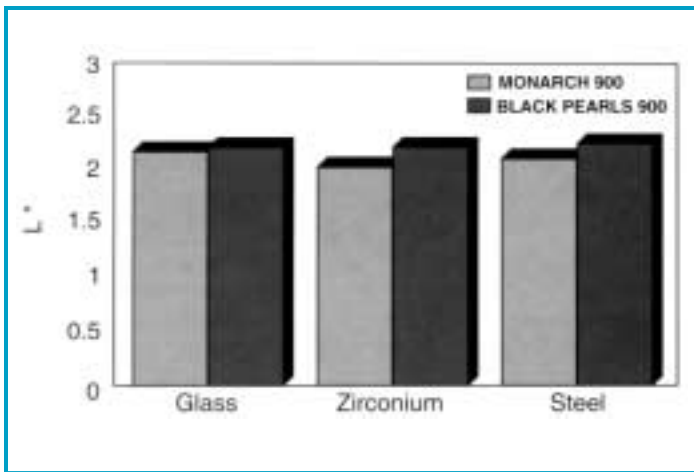


FIGURE 8.

Jetness comparison of MONARCH 900 carbon black vs. BLACK PEARLS 900 carbon black.

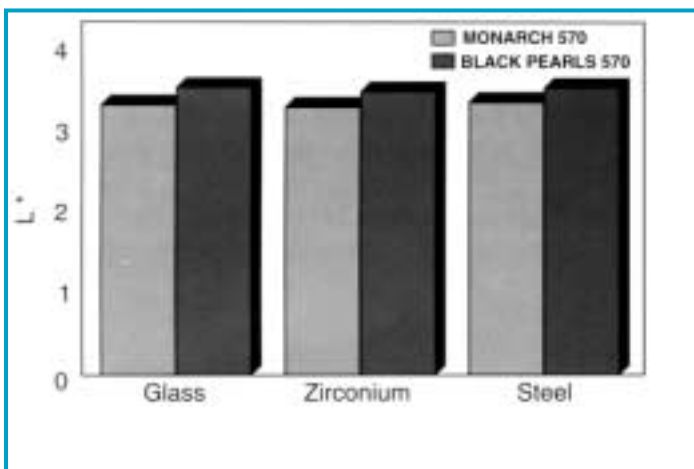


FIGURE 9.

Jetness comparison of MONARCH 570 carbon black vs. BLACK PEARLS 570 carbon black.

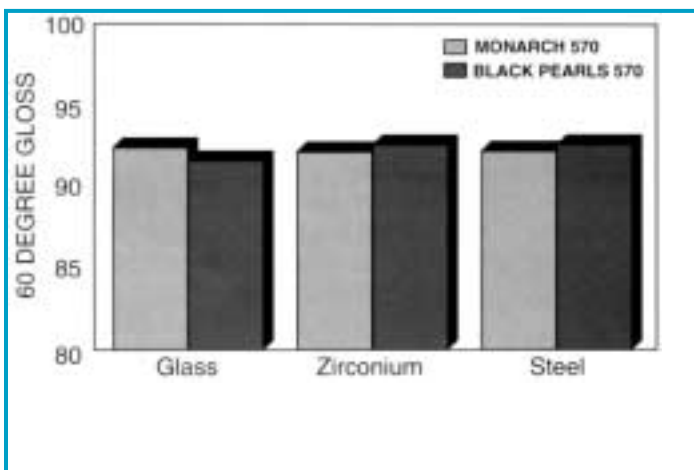


FIGURE 10.

Gloss comparison of MONARCH 570 carbon black vs. BLACK PEARLS 570 carbon black.

CONCLUSIONS

Several conclusions can be drawn from this experiment. When considering only the time required for optimal dispersion, fluffy grades of carbon black disperse more rapidly than their pelleted counterparts regardless of the type of media used. Processors who choose a fluffy carbon black will benefit from reduced dispersion time and a reduction in mill wear. Steel was shown to provide the fastest dispersion, followed by zirconium silicate and glass. Where mills are not designed for use with steel, processors will benefit by choosing fluffy carbon blacks over the more-difficult-to-disperse pelleted grades. When the quality of dispersion is equal there is negligible difference between fluffy and pelleted carbon blacks in color or gloss regardless of the grinding medium used.

REFERENCES

1. Rumpf, H., "The Strength of Granules and Agglomerates," from *Agglomeration*, Knepper, W.A., (editor), Wiley, New York, 1962
2. Medalia, I. and Richards, L.W., "Tinting Strength of Carbon Black," *Journal of Colloid & Interface Science*, Volume 40, Number 2, August, 1972
3. Sheppard, I.R. and Cope, G., "Methods Available For Dispersion Testing," Steele and Cowlshaw Limited, Hanley, England, March, 1963
4. Montes, S.A. and Sifleet, W.L., "Semicon Smoothness by Image Analysis," 90th ICC Meeting, April, 1992, Victoria, B.C., Canada
5. Cabot Corporation, "Carbon Black Dispersion (Technical Report S-131)," Billerica, Mass., November, 1989

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