2014

$CaCO_3$ White Paper

FLEXIBLE INTERMEDIATE
BULK CONTAINER ASSOCIATION

Calcium Carbonate and FIBC's: A Quick Reference Guide

Introduction

The purpose of this paper is to educate the members of FIBCA about calcium carbonate used in FIBC fabrics and how to assess this material when used in the production of outsourced bags. The technical concepts are presented in a FAQ format to make them concise yet easy to understand.

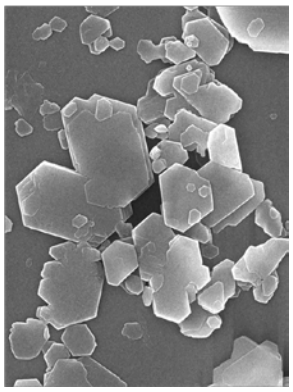
Problem Statement

Uncertainty exists in our industry about Calcium Carbonate ($CaCO_3$) additives used in Flexible Intermediate Bulk Containers, specifically with regards to their potential effect on the performance on fabrics and bags.

The general concern is that any presence of this mineral in extrusion formulas will compromise the mechanical properties polypropylene tape yarn. In reality, calcium carbonate is an additive that is useful and even necessary, provided that it is of the right type and uses appropriate levels. On the other hand, it has been shown that grade and/or content can lead to a degradation of fabric strength and FIBC durability. For this reason it is important to accurately assess the material being added.

Part 1. Technical Discussion

1. What is $CaCO_3$?



Calcium carbonate, or $CaCO_3$, is a mineral rock that is naturally formed from the sedimentation of organic material, primarily marine microorganisms. Because it is so plentiful (making up 4% of the earth's crust) and it is relatively simple to mine, it is an economical mineral to use as an additive.

Calcium carbonate has many useful properties and it is used as a modifier in the manufacture of a broad range of products including paints, coatings, plastics, paper, cosmetics, pharmaceutical and food just to name a few. $CaCO_3$ additives are used to modify a material's characteristics such as texture, color, density, adhesion, gloss, opacity, impact and porosity.

2. Is $CaCO_3$ always used in the production of fabrics for FIBC's?

The addition of $CaCO_3$ in the extrusion formulation provides benefits in quality and efficiency in the production of tape yarn for FIBC's. Used properly calcium carbonate will:

- Prevent fibrillation or splitting of the tapes,
- Allow for higher draw ratio and hence yield higher strengths
- Improve overall extrusion process efficiency.

For this reason it is unlikely that any FIBC fabric is made <u>without</u> any Calcium Carbonate content.

3. How are $CaCO_3$ minerals graded for use in additives?

There are two basic forms of $CaCO_3$: Precipitated calcium carbonate (PCC) and ground calcium carbonate (GCC). In the case of PCC, superfine grades of calcium carbonate crystals can be engineered by precipitating lime from a slurry called slake. GCC, the most common form of calcium carbonate, is made from progressively grinding large rocks of naturally formed limestone down to smaller particles. This is achieved through several successive stages to assure highest uniformity of particles. GCC particle sizes are most typically from 50 microns down to less than 1 micron in size. Because ground particles tend to be irregular in shape, particle size is normally compared by their equivalent spherical diameter (ESD).

When $CaCO_3$ is ground into smaller particles, a range of sizes is produced. The particle size distribution (PSD) is an important measure of the range of particles in the mineral additive and it indicates the quantity or percent of the particles at various sizes. When comparing ground $CaCO_3$ materials, we not only want to know the average particle size known as the d_{50} but also what the largest size is accounting for less than 10% of the total particle count. The latter is known as the top cut or the d_{90}.

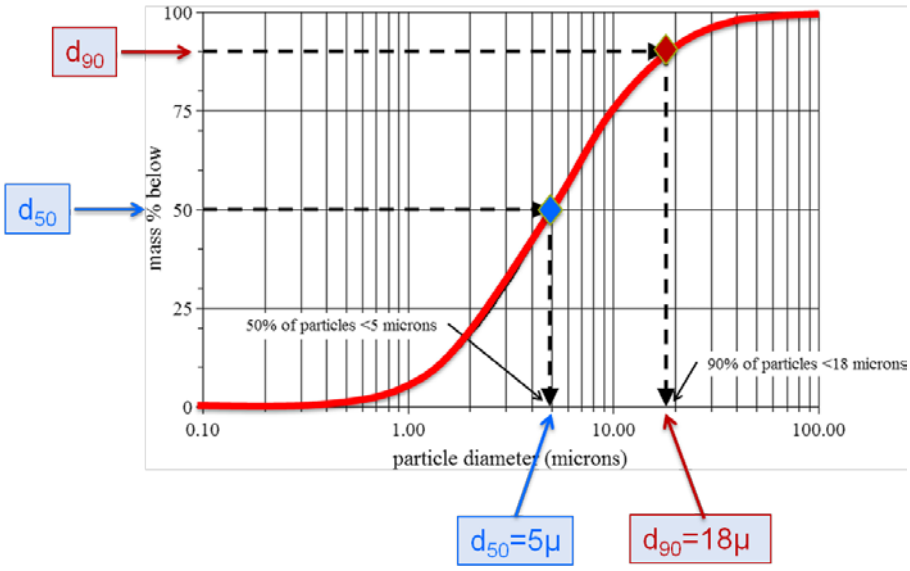


Figure 2. Example of a Particle Size Distribution graph for a d50=50 microns.

4. So what is a "good" $CaCO_3$ additive for FIBC fabrics?

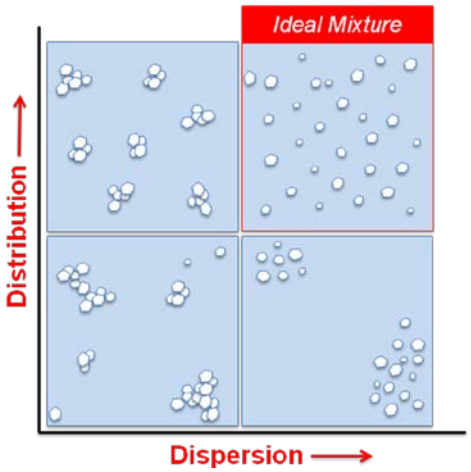
It is well known in the art of polypropylene extrusion that adding appropriate amounts of calcium carbonate in the polypropylene extrusion formula contributes to the properties of tape yarn. Extrusion trials of various particle sizes at various concentrations show that there is an increase in tensile properties when a fine grade of this mineral is added to the virgin formula in appropriate amounts, specifically when:

- Ground calcium carbonate has an average particle size in the range of 1-3 microns ESD
- Particle size has a top cut preferably in the range of less than 10 microns,

Caveat: These results are for the materials and conditions evaluated and are not intended to represent absolutes; your own results may vary.

5. How is $CaCO_3$ introduced into fabrics for FIBC's?

In order to obtain the desired property improvement when such a small quantity of mineral being added to the extrusion formula, it is critical that particles be fully dispersed and uniformly distributed into the PP. There are three important considerations: First, when fine grades of 1-2 micron average particle size are used they should preferably be coated with a stearic acid to prevent agglomeration (the tendency of particles to stick together). Secondly, the ground $CaCO_3$ mineral should be compounded into a resin pellet with either a PP or PE carrier (of high melt flow), preferably in a loading of 50-75% (Note that it can also be included in a formulation for a color concentrate). Lastly, these compounded pellets should be accurately dosed with the virgin PP during extrusion. This is achieved with a programmable gravimetric dosing unit feeding into the extruder. Any form of non-automated addition and even batch mixing (pre-mixing off line) can result in poor distribution of mineral potentially creating weak regions in the drawn tape yarn.



Part II. Getting Informed

1. Questions to ask the fabric producer?

What percentage of calcium added to master batch?

- Is it coated?
- What type of calcium is used?
- What is particle size?

Review procedures for introducing it into master batch and extrusion.

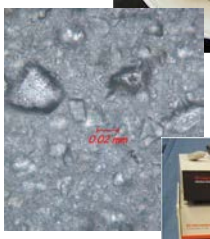
- Is it mechanical or done by hand? Please discuss.
- What methods are used to guarantee it is added?
- What training is given to employees in this area?

Are regrinds used?
How is dosing done?
What documentation do you have to prove the percentage in final fabric sample?
What performance tests do you have for this fabric?

2: What tests are available to verify expected and proper $CaCO_3$ usage?

There are two types of testing that can be done to check the quantity and quality of the $CaCO_3$ that is present in FIBCs.

1. To check the amount of $CaCO_3$ in your FIBCs the following tests are available.
    a. Ash test - This test basically burns off everything except the minerals present. This is done by a 600 degree C oven. Weight of ash divided by the weight of the original sample, tells you the $CaCO_3$ percentage. (There will be small amount of other additives in here, however the majority should be $CaCO_3$. This test method uses ASTM D5630-13. A FTIR (Fourier Transform Infrared Spectrometry) can be used after the ash test to verify the materials remaining. This test uses ASTM E168. The ash test can and should be run on a regular basis to guarantee that your suppliers are putting the percentage of $CaCO_3$ that you have agreed to, in the fabric.



    b. X-Ray Fluorescence Spectrometry- this test is basically a hand held gun that tells you the percentages of each type of mineral in the fabric.
2. Checking the PSD (particle size Distribution) is important for making sure the $CaCO_3$ is not only the agreed upon size, but that is also mixed properly.

    a. CILAS- Use the principle of laser light scattering to measure the particle size. If the particle size is to big then you may not get dispersion and you may still have issues, even though the percentage of $CaCO_3$ is what you agreed to.
    b. SEDIGRAPH- By using Stoke's law, particles size is determined by measuring the rate (speed) at which a particles of known density settle in a fluid of known viscosity.
    c. Film Transparency Micrograph - A thin film is pressed from the subject resin and then viewed at 100x to 500x magnification to assess particle dispersion and distribution.

Part III. Conclusion

FIBCA is not recommending specific particle size or $CaCO_3$ percentage that your company chooses to put into your bulk bags. However from the information displayed above, you can see that the selection of the type, size, distribution and percent used of the $CaCO_3$ are important to the performance and long term reliability of your fabrics.