MICHAEL WHALEN-SHAW, Ph.D.
7041 Zane Trail Road • Circleville, Ohio 43113
(614) 474-1129 • FAX (614) 474-2625

DOE/CE/15602--T4

January 23,1997

Mr. Fred Hart
Department of Energy ,CE 521
1000 Independence Ave. S.W.
Washington,DC 20585

Subject: Final Technical Report on DOE Grant Number DE-FG01-94CE 15602, Replacement of Thermally Produced Calcined Clay with Chemically Structured Pigments and Methods for the Same

I. Introduction

The objective of work under this grant was to provide a sufficient and convincing body of data to entice a company to partner with the inventor and take a license to work toward commercialization of this technology.

The replacement of calcined clay pigment which is used for opacification in many applications including paints, ceramics, paper coating and paper filling. The basic process of the instant invention involves a charge neutralization of two particles of opposite charge and requires only the energy of mixing. This results in a potential savings in achieving opacification of about $5.5 to 12.5 MM per year over using calcined clay.

The resultant combination of two non-identical particles is termed a layered pigment. This investigation focuses on layered pigments for the paper industry and more specifically layered pigments for paper coating

II Summary of Results Relating to Theory

Combinations of cationic titanium dioxide and standard hydrous clay produce a structure which is unique in three respects.

Firstly, it was found that a certain amount of titanium dioxide did not react with clay to form a layered pigment. However, the unreacted titanium dioxide was found to be much more dispersed (and therefore much more efficient for light scatter than if it had been homoflocculated) than a simple blend of standard anionic titanium dioxide and anionic clay. It is believed that some of the cationic TiO_2 combines with anionic clay dispersant (

BD - Final

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

MICHAEL WHALEN-SHAW, Ph.D.
7041 Zane Trail Road • Circleville, Ohio 43113
(614) 474-1129 • FAX (614) 474-2625

sodium polyacrylate) to produce an anionic TiO2 with an expanded double layer which is more resistant to homoflocculation.

The second unique aspect of the resulting structure was seen (with the electron microscope) to be the physical attachment of TiO2 to the clay surface. This also results in improved light scatter because the TiO2 particles are separated from their nearest neighbor by clay particles. The close proximity of TiO2 and clay particles provides a change in refractive index of light which causes light scatter and an increase in opacity.

The third unique aspect of the resulting structure is an increase in the amount of void volume in the final structure. This was repeatedly shown by increases in the wet void volumes of the precipitate resulting from centrifugation compared to standard anionic blends of the two pigments.

Thus, the above mechanisms combined to produce a layered pigment exhibiting improve opacity.

III. Results on Coated Paperboard

The work plan for this investigation specified that the layered pigments would be evaluated in a variety of paper applications. Early on, it was realized that the companies who might license this invention required an overwhelming body of data to be convinced. Further, it was realized that the greatest opportunity was in an application using the highest level of TiO2 and calcined clay. For this reason brown paperboard , such as that used in beer cartons , was chosen as the substrate and coatings using a plethora of different layered pigments were evaluated. A large body of performance data has been supplied in quarterly reports.

Crucial data relating to the substitution of layered pigments for calcined clay on coated natural kraft are as follows.

1. At a high TiO2 usage level, such as 30% of the total pigment, the brightness of coated board for 5,10, and 15 % calcined clay is 78.0, 79.4, and 79.8 , respectively. (Note: the balance of the pigment is standard #1 clay and the coatweight is 3.5 lb./1000 sq.ft.)

MICHAEL WHALEN-SHAW, Ph.D.
7041 Zane Trail Road • Circleville, Ohio 43113
(614) 474-1129 • FAX (614) 474-2625

2. The layered pigment containing 30% Ti02 and 70% #1 clay yields a 79.2 brightness. This allows the complete elimination of calcined clay when it is used at the level of 10% of the total pigment.

3. Some manufacturers use up to 15% calcined clay in their board coatings. Engineered clays, which are particle size fractionated clays, provide higher opacity and brightness than standard non-fractionated clays.. Engineered clays were therefore investigated as components of layered pigments to improve their performance in the replacement of calcined clay. Specifically, a layered pigment containing 30% TiO2 and 70% Eclipse 5200 engineered clay gave a coated brightness of 81.3. This level of brightness provides not only the opportunity to eliminate 15 parts of calcined clay but also to reduce TiO2 by 6 parts. The loose blend of 30 % TiO2 and 70% Eclipse 5200 gave an 80.3 brightness, enough to replace 15 parts of calcined clay but not to reduce Ti02.

Economic considerations reveal that the pigment cost/cwt necessary to achieve a final coated board brightness of 80.0 for the control coating containing 30% TiO2 , 15% calcined clay, and 55% #1 clay is about $36.10. The cost of a 30% TiO2 and 70% Eclipse 5200 blend is about $37.00. Obviously, there is not incentive for either a clay company or its customer to make a change. However, the raw material cost for the layered pigment which will give also an 80 brightness and contains 24 TiO2 and 76 Eclipse 5200 is $31.60/cwt. Unfortunately, when processing costs and development costs are added in this does not provide enough cost incentive to the customer , albeit a drop in TiO2 usage from 30 to 24 parts and complete elimination of calcined clay. The reason is the high cost of the engineered pigment Eclipse 5200.

IV Business Considerations

A product development relationship was formed with Dry Branch Kaolin Co. They evaluated the present technology and found a 2.7 brightness improvement at the 10 part TiO2 level using standard #1 clay. This was better than the author found. In spite of these promising results. work has been temporarily discontinued due to the company entering into a new venture which required all of their development time.

MICHAEL WHALEN-SHAW, Ph.D.
7041 Zane Trail Road • Circleville, Ohio 43113
(614) 474-1129 • FAX (614) 474-2625

Subsequently, a presentation of the huge body of data generated under this grant was made to Engelhard Corporation. This has resulted in a developmental license being issued to them. Their evaluation of the layered pigment technology has shown a consistent 2 point brightness improvement over controls. The author has, in some cases, seen 4-5 points improvement. A search for the reason for sometimes good performance vs sometimes outstanding performance is underway. Further work will center around making standard clay give high performance so that the cost advantage of replacing calcined clay and reducing TiO_2 will stand out to the clay manufacturer and the customer.