From "Dust" to Quality Dielectric—The Formulation of Dielectric Clays

Key Words: Kaolin clay, calcination, silane treatment, compound formulation, fillers, ethylene propylene rubber (EPR)

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The incorporation of silane-treated clays in EPR-based compounds results in greater volume resistivity and higher dielectric breakdown strength as required for medium and high voltage insulations.

Introduction

Early in electrotechnology, the insulation material of choice was a braided, varnish-impregnated cotton or linen fabric wound directly onto the copper conductor. This worked very well for low voltage (<600 V) and was employed for both distribution and internal wiring in homes using standoff insulators (knob and tube). This dielectric was replaced first by latex rubber insulation, then by strip-insulated rubber (calendered rubber strips that were heat sealed and vulcanized onto the conductor), and finally by extruded rubber-insulated cable. The compounding of these rubber materials used clays as stiffeners and fillers to enhance mechanical strength and employed wax and tar-impregnated cotton braids as overall jackets. These were still unshielded, low voltage cables.

As the need for power increased, the electrical industry looked to increase the voltage to reduce losses. Natural rubber was replaced with styrene butadiene rubber (SBR); SBR was replaced by butyl rubber; and, finally, butyl rubber was replaced by EPDM and XLPE as the voltages rose from 5 to 15 to 35 to 138 kV. In each of these steps, the rubber compounds required clay initially to enhance mechanical properties, later to improve electrical properties, and finally to give the excellent physical and electrical properties we now know and use. As a result of this evolution, the clay manufacturers responded with purer, more controlled materials to assist in meeting the challenge.

What is Kaolin Clay and How Is It Converted to Electrical Grade?

We will now define Kaolin (clay), describe where it comes from, how it is processed, and its range of uses as the material is converted from "raw earth" to a highly engineered, functional component of medium and high voltage insulations.

Clay is defined chemically as hydrated aluminum silicate—$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ or $Al_2Si_2O_4$. It is 37% (w/w) Al_2O_3, 45% (w/w) SiO_2 with trace impurities of TiO_2, Fe_2O_3, and Fe_3O_4. The crude clay is pit-mined, crushed, and separated according to the end-use (Figure 1).

A) Hard or Soft Clay, Air-Floated or Water-Washed Clay

In the early part of the twentieth century, clay was divided into hard and soft clay. These nomenclatures referred to the modulus (reinforcing) properties of the material in natural rubber. Most clay was air-floated or water-washed to remove impurities and to adjust particle size.

Air-floated clays are subsequently attrition-ground to reduce 325-mesh oversize and improve dispersion. The particle size distribution of the air-floated products is dependent on the naturally occurring mineral, as no processing is conducted to alter it from that found in the deposit.

Air-floated clays are poorer in color (~GE brightness, 75 to 82) and exhibit higher LOD (loss on drying), ~1.0%; higher crys-

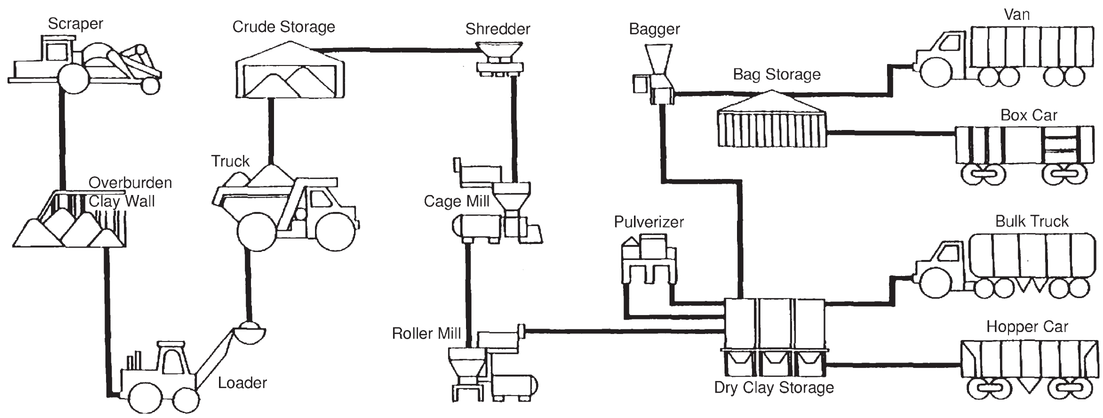

Figure 1. Typical air-flotation process.

talline bound water (~14%); higher 325-mesh residue, ~0.05 to 1.5%; and variable particle size distributions. Use of air-floated products is restricted to jacketing and low voltage applications because of these deficiencies.

Water-washed clays are processed first by crushing the crude clay, mixing in a water suspension with appropriate dispersants, centrifugally classifying into specifically defined particle size fractions, bleaching, and subsequently filtering to remove solubilized iron (Figure 2). In addition, the suspension may be subjected to high intensity magnetic separation to remove paramagnetic (weakly magnetic) particles to increase the brightness. The "slurry" is then spray-dried into soft dispersible agglomerates. These spray-dried clays are used extensively in paper filling/coating applications, as well as spacing TiO_2 in various coating applications. Water-washed clays contain ~14% water of hydration (crystalline bound) and ~1.0% free moisture and have higher GE brightness (84 to 91). The spray-dried clays may be attrition-ground to lower the coarse fraction, 325-mesh residue and to improve dispersion. The purity level of the water-washed kaolins facilitates their use in low voltage applications and internal stock for high voltage insulators and stand-offs.

B) Calcination

Water-washed hydrous kaolin is introduced in a "calciner" that is thermally exposed for a specified time and at a temperature sufficient to remove ~99.5% of the water of hydration, thereby altering the crystalline phase and improving the insulation properties (Figure 3). The calcined kaolin is cooled and processed further to improve dispersion and is then used as a vital constituent in filled PVC compounds to improve electrical performance. European-based PVC compounds containing calcined kaolin are utilized in cable construction up to 5 kV. Calcined kaolin typically exhibits very low loss on ignition @ 980°C ~<0.15% and has an amorphous structure (Figure 4).

Compounds with In Situ Surface Compatibilization

Calcined clays are intermixed with various rubber dielectrics through in situ addition of various silanes to enhance compatabilization. Most of these compounds are used at <5 kV, though some have been used in electrical utility cables operating at 15 to 35 kV.

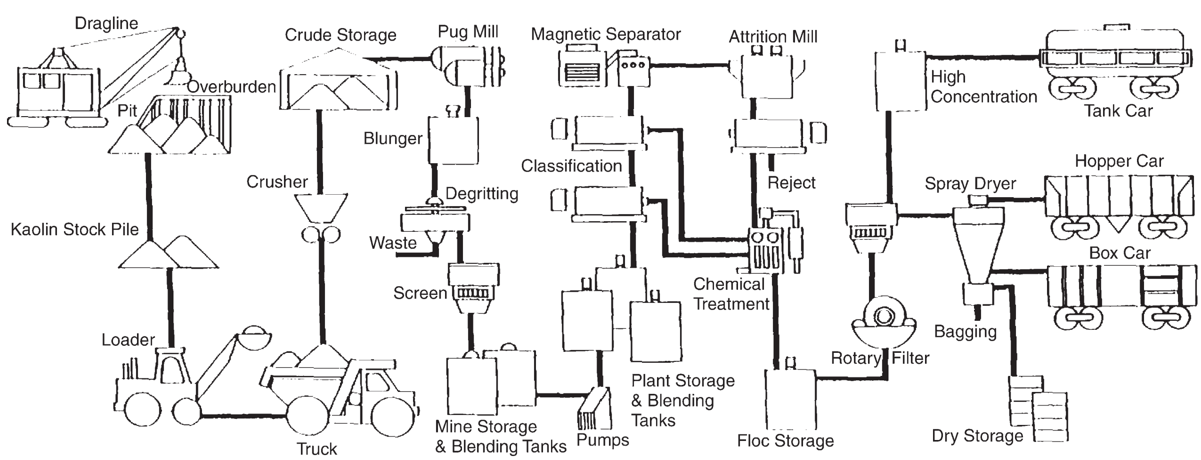

Figure 2. Typical water-wash process.

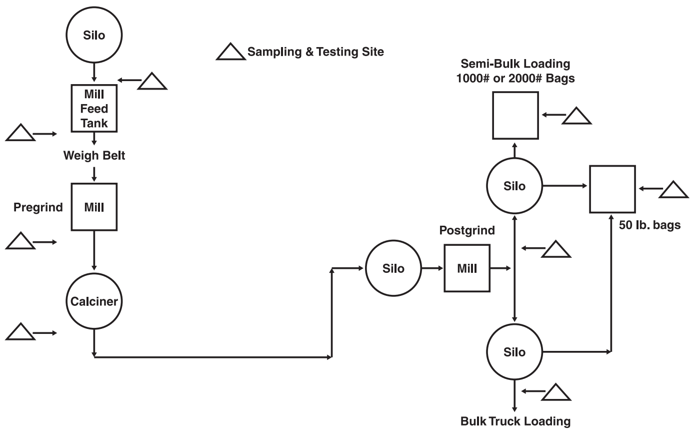

Figure 3. Typical calcined-clay process flow schematic.

A) Surface Treatment of Calcined Kaolin Clay

Calcined kaolin clay is the feedstock base for the highly engineered “treated clays.” Calcined clay is introduced into a reaction system with an organo functional silane and is chemically reacted under controlled conditions (Figure 5). The reaction process results in the formation of Si-O-Si bonds coupling the kaolin and silane. The functionalized silane then reacts with the polymer binding the once incompatible phases into a dynamic electrical insulation compound. The amorphous structure is still maintained after reaction with an appropriate silane (Figure 6).

Quality Control

The process in which the silane is reacted with the calcined kaolin clay is precisely controlled. The final product is subject to a variety of tests prior to, during, and after treatment to ensure the integrity of the process.

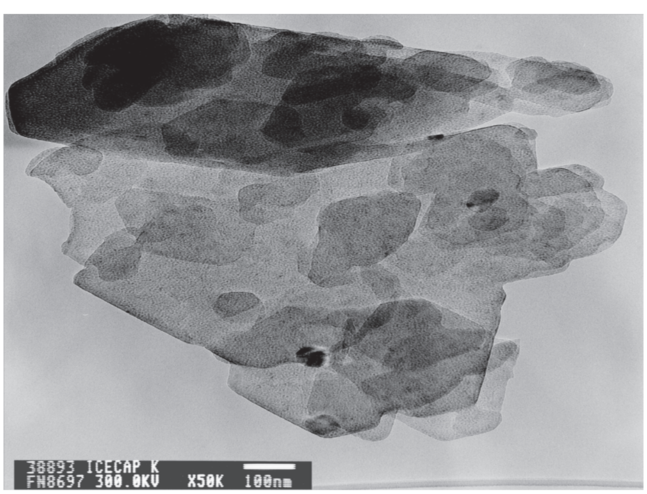

Figure 4. Photomicrograph of calcined clay.

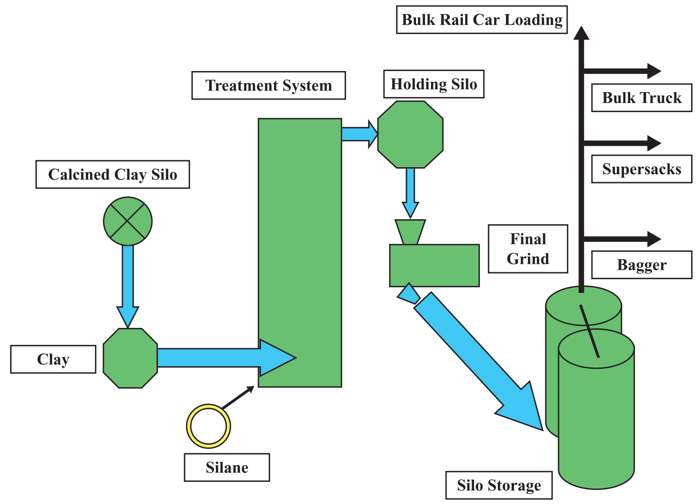

Figure 5. Silane-treatment system.

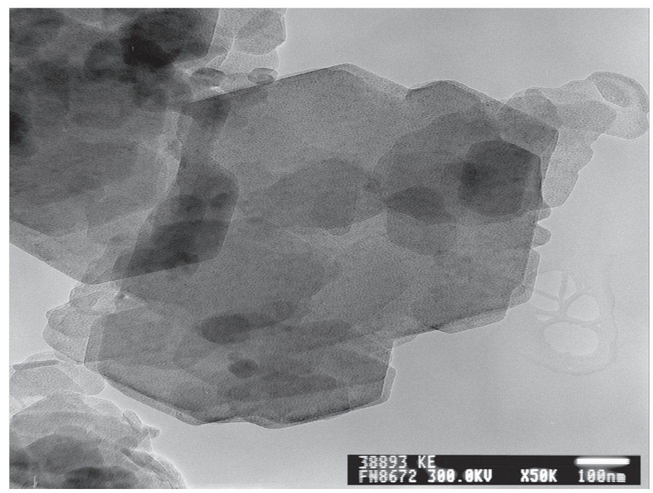

Figure 6. Photomicrograph of silane-treated clay.

Table 1. Model EPR compound formulation.

Base Compound	phr
EXXON Vistalon 2504	100
Pb_3O_4-90% Dispersion in EPR	5
Zinc Oxide	5
Agerite Resin D	1.5
Clay	60
TOTAL	171.5
Vulcanization Package	
Base Compound	100
DiCumyl Peroxide (40% dispersion)	3.6
TOTAL	103.7

Table 2. Properties of model dielectric.

Test	Tensile Strength (psi)	Elongation to break (%)	200% Modulus (psi)	Volume Resistivity (ohm-cm)	AC Dielectric Breakdown (V/mil)
Material					
Hydrous Clay	876	306.9	680	4.47e14	438
Calcined Clay	830	309.6	602	6.4e15	502
Silane-Treated Clay	1224	307.5	935	1.83e16	725
Burgess KE Clay	1478	209	1397	1.59e17	872

Compound Formulation

Having now made and treated the clay, we will now discuss briefly how this material is applied to shielded power cables. Compounding of such insulation will be described in a future article and has also been addressed in [1].

At our company, we use a common EPR cable dielectric formulation to check our treated clays, develop new silanes/silane sources, and monitor the process and process changes (Table 1). This very basic formulation helps to focus on changes in dielectric and mechanical properties caused by the clay. All testing is carried out per ASTM D-149 (Electrical) and D-412 (Physical) (Table 2).

From the physical point of view, the 200% increase in the modulus demonstrates the increased interaction of the treated clays with the rubber matrix. As the functionality and bonding of the silane to the polymer increases, so also does the modulus. This results in increased modulus and an increased tensile strength. For untreated clay, the increase in modulus would only be attributable to the particle size (fill ratio). Thus, the treated clays reinforce the polymer by cross-linking into the system, whereas the non-treated clays only support and "fill" the structure.

From an electrical perspective (Table 2), the effect of water removal is quite clear between the hydrous and calcined clays. Removal of the water through calcinations increases the resistivity of the resulting compound by about one order of magnitude. As previously stated, hydrous clays can be used as fillers for low voltage applications. The incorporation of silane-treated clays in EPR-based compounds results in greater volume resistivity and higher dielectric breakdown strength as required for medium and high voltage insulations. The high purity of these materials, increased hydrophobicity, and increased reactivity with the base polymer result in treated clays being more than "just fillers."

To summarize, the "Glacier's Gift to Georgia" has been removed from the earth, ground, and cleaned; its water and contaminants were removed and chemically modified. The resultant product was made such that it can be used as an integral and essential part of the distribution cable technology available today.

Acknowledgment

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References

[1] M. Brown, "Compounding of ethylene-propylene polymers for electrical applications," *IEEE Elec. Insul. Mag.,* vol. 10, no. 1(Jan./Feb.), pp. 16–22, 1994.

John D. Hogan received his degree in chemistry from St. Francis and continued post graduate studies at St. John's University and NYU. He has held various senior management positions in R&D and Manufacturing in the Rubber and Plastic industry, specifically in Wire and Cable with Pirelli and Phelps Dodge. He has authored papers, lectures, and articles regarding compounding, methods, testing, and techniques used in the rubber and plastic industry.

Lewis Berry currently holds the position of Technical Director of Burgess Pigment Company and has 30 years experience in manufacturing of calcined and surface-treated kaolin clays.