clay: the all-purpose rubber filler

I know you may feel like clay is a tired, worn-out subject. But before tossing this aside as old news, there are a number of unique clays with which a rubber compounder should be familiar. There are many ways to use clay's excellent cost and solve problems as well. Unfortunately, when I refer to clay usage in rubber, an associate of mine has a favorite expression: "Hey, it's just dirt *you're selling." Yes, clay (often referred to as "kaolin" after a region in China where clay was mined centuries ago) is a mined product but it is much more than simple dirt. Clays have become widely used in rubber from inexpensive car mats to hypercritical high-voltage couplings. They offer some of the best cost/performance ratios of any available rubber filler. That's why, next to carbon black, clay [aluminum hydroxide silicate, $Al_2(OH)_4SiO_5$] is the most widely used filler in rubber compounds. Clay prices are not tied directly to oil prices unlike most synthetic polymers, carbon black, and petroleum oils. Akrochem has clays to offer from low-cost, high-loading soft clays to the ultimate "cleanest kaolin in the world" – Huber products designed for the power cable industry.*

kaolin clays

Almost all the top-quality clay used by the U.S. rubber industry comes from the "kaolin belt" that is found in South Carolina and Georgia. Typically, these deposits yield clays of 90% or more aluminum hydroxide silicate. The remaining non-kaolin constituents consist of a cornucopia of metal oxides including iron, titanium, calcium, magnesium, potassium, sodium and possibly manganese. This is the "dry portion" of kaolin clay.

Kaolin also contains about 14% water. Most of this moisture is bound and is lost only at very high temperatures (loss on ignition, LOI, tested at 950°C). Free moisture, on the other hand, is usually less than 0.8% at the time of production. True kaolin clays are not very hygroscopic and therefore will not absorb excessive moisture (typically less than 2.0% total free moisture even in high-humidity conditions – as a comparison, silicas contain about 5.5% free moisture as manufactured). Adding calcium oxide to your formula because you suspect clay is causing blisters due to moisture is often the wrong way to go.

air-floated clays

The simplest clay used by the rubber industry is termed air-floated clay because the clay is sized by air classification. Air classification removes much of the non-kaolin materials and results in a minute 325 mesh screen residue (typically less than 0.35%). These air-floated clays are divided into two major categories: soft clay and hard clay.

Hard clay and soft clay are basic descriptions of the result of adding these fillers to rubber. Akrochem's hard clay, **HC-75**, is composed of greater than 90% particles less than 2 microns. Thus it is more reinforcing and results in a higher durometer (rule of thumb is 4-5.5 phr per durometer point increase), higher modulus, tear, and tensile than soft clay. For its low cost, hard clay provides an extremely high amount of reinforcement. Decent abrasion properties are available even in very low-cost formulas.

Compounding techniques can help make useful, low-cost formulas with hard clays. Usually, sulfur and primary, as well as secondary, accelerator levels should be increased to insure a tight cure. Mill sticking can be a problem with highly loaded hard clay batches. Try a mill-release process aid like Proaid AC 18-DSA before giving up on the low- cost clay. Mold release can be greatly improved with 5 phr loading of LMW polyethylene wax.

Soft clay usually contains less than 70% particles under 2 microns. Whereas hard clay will increase the viscosity of rubber compounds, soft clay loading will have little effect on viscosity and thus offers a large improvement in the processing of rubber. Compare the extrusion rates of a hard clay-loaded formula vs. a soft clay loading:

EXTRUSION RATE VS. LOADING OF AIR-FLOATED CLAYS

PHR OF CLAY	Extrusion Rate, cc/100 sec	
	HARD	SOFT
25	118	138
70	106	136
105	94	136
130	83	136
160	78	135
180	59	132
210	38	122

The minimal effect on processing properties by soft clay is evident in this graphic.

Akrochem's **SC-25** soft clay will reinforce moderately (rule of thumb is about 5-7 phr per duro point increase) and will have minimal effect on compound viscosity. This allows soft clays to be used at extremely high loadings for cost reduction and maintain a workable compound. Extrusion properties are much better than hard clays. Mill and mixer sticking are much less of a problem with soft clay than with hard. So those applications that do not require abrasion resistance or other higher-quality reinforcement properties should look at soft clay for cost reduction and good processing with modest reinforcement (use calcium carbonate for cost reduction with no reinforcement). It is interesting to note that soft clay-type deposits are limited in the U.S. while the opposite is true in Europe. For this reason, soft clay usage is more prevalent in Europe.

EW-150 is a brighter and more consistent-colored hard clay at almost no cost difference.

GRADES:	HARD CLAY EW-150	HARD CLAY HC-100	HARD CLAY HC-75	SOFT CLAY SC-25
Free Moisture	0.65	0.70	0.70	0.80
Ignition Loss, %	14.0	14.0	14.0	14.0
GE Brightness	80	77	77	79
Particle Size, <2μ	92%	92%	92%	68%
Mean Particle Size, μ	0.3	0.3	0.3	1.2
Screen Residue, % (325 mesh)	0.25	0.25	0.35	0.35
pH	4-5.25	4-5.25	4-5.25	4-5.25

water-washed clays

Water-washed clay is a simple term used for what is, in essence, a thorough cleaning of the kaolin clay. This includes degritting, magnetic separation, a brightening process, and filtration before preparing for final form. Water-washed clays offer several distinct advantages:

- Extremely low 325 mesh screen residue (0.005% typical)
- High brightness (90+ available) vs. air-floated's 77-80
- Neutral, consistent pH (imp. in peroxide and many sulfur cures)
- Low soluble salts
- Very low alpha quartz
- Processing resembling soft clay with hard clay-type reinforcement*

  [*In the extrusion rate study described previously for soft and hard clay, a water-washed clay at 210 phr extruded at 99 cc/100 sec.]

The low alpha quartz virtually eliminates the hazard of breathable crystalline silica. The low screen residue means less extrusion die buildup from grit like mica. The low salts result in lower water absorption as well as less swell of a rubber compound exposed to water. The removal of iron oxides improves color such that clean, white clays of brightness over 90 are available. This allows brighter colors to be made at lower color costs.

The neutral pH water-washed clays provide consistent crosslinking. **Air-floated clays are acidic and if used with peroxide will often result in a poor cure or even worse, no cure.** Sulfur cures can be erratic depending on the pH of normal kaolin clay. Just like an acid retarder, acidic air-floated clays will slow a sulfur cure. Neutral pH found in water-washed clays prevents these problems allowing peroxide cures to proceed normally as well as sulfur cures with reduced variability and faster cure rates. Less accelerator may be used with water-washed clays because the cure is not retarded.

Consistency is the main attribute of water-washed clays: consistent cures, consistent rubber physical properties (due to tighter particle size distribution control), consistent processing, and finally, consistent, clean color.

A few examples of water-washed clay follow here. The **Polyfil XB** clay is a very **cost-effective**, water-washed type. If you are interested in trying these cleaner, more consistent clays but cost is a critical issue, try the XB.

An interesting water-washed clay is the **Polyfil DL**. This is a "delaminated" clay. Normal clays exist as stacks of "plates." Delamination splits these plates into individual platelets. This results in several unusual rubber properties along with the typical water-washed attributes of good color, low grit and neutral pH. Compared to air-floated hard clay, here are some differences that Polyfil DL offers:

- Higher modulus, hardness, and stiffness than regular hard clay.
- Higher rebound than hard clay. Typically, more reinforcing fillers hurt rebound.

- Less die swell than hard clay makes low-cost calendaring and extrusion stocks process better. Better gauge control; less sag and distortion. Good replacement for talcs with similar low viscosity buildup but better scuff resistance.
- **Reduced gas permeability.** High aspect ratio creates a barrier to permeation by gas vapor. This is important from inner tubes to gas masks to gasoline hoses. Fuel C/methanol vapor transmission was 30% lower with Polyfil DL than with hard clay in an NBR formula. Water vapor transmission was improved over a talc-loaded formula. Mustard gas permeation resistance in a Polyfil DL-loaded gas mask was improved over the previous silica/clay loading (exact results considered proprietary).
- **Polyfil DLX** is a similar platy clay but with a higher aspect ratio to improve the permeation resistance even further. The larger particle size builds viscosity slower, allowing higher loadings and tighter packing.

*[We have only recently been apprised of a new product being offered by Huber that may offer unusual permeation resistance. The product is called "**HuberGuard**™" and is a material designed for chemical-resistant epoxy coatings. It has a very platy structure but a low surface area. This allows very tight packing of the filler with high loadings possible due to minimal viscosity increase. This is a designed mineral product that will function similar to Polyfil DL with possible superior permeation resistance. HuberGuard is also very hydrophobic which can be useful for corrosion resistance and low water uptake. Product is too new to have even been tested in rubber. May be something to look at in gasoline hoses, air bladders, propane gas lines, etc. HuberGuard comes in two grades: **SH-100** and **CA-100**. SH-100 is the more platy. CA-100 is more "blocky" and lower in oil absorption (permits higher loadings).]*

Another useful water-washed clay is the **HG-90**. The properties match hard clay for reinforcement in all respects but the brightness allows very clean, vibrant colors to be produced. In many cases where a light color like a white or yellow is needed, the cost of coloring HG-90 is significantly less costly than making the same color with air-floated hard clay.

Water-washed Clays:	DL*	DLX*	F/FB	X/XB	35	HG-90
Brightness (% reflectance)	88	88	88	87	82	91
pH (28% solids)	7.0	7.0	6.8	6.8	6.8	8.0
Med. Particle Size (μ)	1.0	6.5	0.6	0.7	4.0	0.2
Surface Area (m^2/g)	13	12	15	14	9	22
325 Mesh Screen Residue %	.01	.05	.005	.01/.005	.05	.01

*delaminated clays

treated water-washed

Chemically modified clays can offer numerous improved properties over standard hard clay and water-washed clays. To produce chemically modified clays, the water-washed clays are treated with a dual functionality silane. One end bonds to the clay surface; the other end will couple to the polymer. Huber/Akrochem offers four versions of mercaptosilane-treated clays for sulfur cures. These range from the very economical Nucap 100G with lower silane treatment and moderate brightness up to Nucap MX with high brightness and maximum silane treatment. The properties bulleted here are improved by silane treatment and as silane level increases, these properties usually will also improve:

- Improved tensile, tear, and modulus properties. Modulus will continue to increase with higher silane levels. Tensile and tear will reach a peak and level off.
- Improved compression set, permanent set, and heat buildup resistance (lower hysteresis)
- Improved processing due to better dispersion and lower viscosity
- Improved adhesion of rubber to other materials
- Reduced water pickup for clay in storage and in clay-loaded formulas

Pretreating these water-washed clays with silane instead of adding free silane to a mix that contains hard clay results in a more consistent product that mixes quicker with improved physical properties. *One oft-forgotten factor – silanes are very water sensitive. If you add silane at the banbury, great care must be taken to use fresh, unexposed, free silane or risk no reaction with the clay. Pretreated clay ties up the water-miscible end of the silane and thus makes the pretreated clay/silane combination extremely stable.* Many a compounder has struggled to get good performance out of clays and/or silicas when adding silanes. This is sometimes due to the silane having been deactivated by water hydrolysis.

Here's a simple example of the improved properties provided by a silane-treated clay. A synthetic polyisoprene formula had 75 phr of hard clay added and 75 phr of Nucap 190 with the following results:

Physical Properties	Hard Clay	Nucap 190
300% modulus, Mpa (psi)	5.31 (770)	**12.21** (1770)
Tensile, Mpa (psi)	21.24 (3080)	22.34 (3240)
Elongation, %	580	480
Hardness, Shore A	59	64
Compression Set, 22/70C, %	30	**14**
Tear, Die C, kN/m (ppi)	27.1 (155)	**41.1 (235)**

[Natsyn 2200 – 100, Clay – 75, ZnO – 5, Stearic – 2, Sulfur – 2.75, OBTS – 1.15, TMTD – 0.2]

While tensile is only mildly enhanced with the silane-treated clay, the crosslink density is vastly improved based on the modulus and compression set data. Even more interesting is the improvement in tear. In most curing systems that increase crosslink density, tear is adversely affected. Usually as modulus goes up, tear goes down. Yet in study after study, the silane-treated clays yield better tear along with tighter cure properties.

Mercapto silane is typically used with sulfur cures although the mercaptos give a decent response even in a peroxide cure; vinyl silane is typically used with peroxide (for vinyl treated clays, see Treated Calcined Clays); amino silane can be used with sulfur or peroxide. Not only do these treated clays offer physical properties resembling semi-reinforcing carbon black, but the high brightness means clean, rich colors at lower color loadings.

GRADES:	Nucap 100G	Nucap 190/M	Nucap 290/M	Nucap MX	Nulok 390
Silane Treatment	Mercapto	——Increasing Mercapto silane		——→	Amino
Brightness (% reflectance)	88	91	91	91	91
pH (28% solids)	7.0	5.8	5.8	6.5	8.7
Med. Particle Size (μ)	0.2	0.2	0.2	0.2	0.2
Surface Area (m^2/g)	22	22	22	22	22

calcined clay

Water of hydration in kaolin clay is about 14%. Heat-treating, or calcining, eliminates this water and creates a unique kind of clay.

- Excellent processing. Smooth extrusions; low viscosity even at high loadings; no stickiness on mills or in mixers.
- High brightness; clean bright colors are possible.
- **Very good compression set in non-black formulas.** Only silane-treated, calcined clays are better for set properties in colored compounds.
- Excellent electrical properties. Again, only treated calcined clays are better. Calcining prevents moisture pickup in storage and in a rubber compound.
- FDA permissible. Treated clays are not FDA.
- Physical properties are reduced with calcining. Heat-treating smoothes the normally rough surface of hard clays. Thus lesser reinforcement, similar to soft clay, is to be expected. Silane-treated calcined clays provide a little better physicals.

Typical Properties	Polyfil Calcined Clays 70	80	90
Brightness (% reflectance)	91	92.5	93
pH (28% solids)	5.5	5.5	5.5
Med. Particle Size (μ)	1.4	1.4	0.7
Surface Area (m^2/g)	8	8	15

treated calcined clays

The premium clay product is calcined clay that is treated with reactive silanes. Because the vast majority of these clays are used in electrical applications where peroxide cures dominate, the silane most used is peroxide-friendly, vinyl silane. These clays are used in some of the rubber industry's most demanding applications. Electrical properties that must remain viable for twenty years require exceptionally clean clay. Huber Engineered Materials produces some of the cleanest, if not the cleanest, clays available to the rubber industry. These treated, calcined clays are used in high-voltage insulation for power cables and connectors. A quick review of the types available follows here:

Polyfil WC – an industry standard. Used in high-quality electrical goods. A study was done comparing WC to another well-known electrical-grade clay:

Formulation: Electrical Grade EPDM	Polyfil WC	*Translink®37
Physical Properties		
Modulus at 100%, Mpa	6.00	6.10
Elongation, %	271	267
Tensile Strength, Mpa	12.20	12.60
Original Electrical Properties, 23˚C		
Dielectric Constant	2.47	2.53
Dissipation Factor (40 vpm, 60 Hz)	0.20	0.26
14 Days 75˚C Water, measured at 23˚C		
Dielectric Constant	2.53	2.53
Dissipation Factor	0.22	0.21

**Translink 37 is a registered trademark of Englehard Corp.*

Polyfil WC-426 – Similar to Polyfil WC but a finer particle size for better reinforcement.

Nylok 170 – Amino silane treated. Can be used in sulfur or peroxide cures. Finds use in unusual applications like polyamide systems.

As with treated water-washed clays, the pretreatment is critical to the consistent properties provided by the silane-treated clays. Coupling the silane to the filler surface is assured (this may not take place when silane is added separately at the mixer). **Treated clay silanes will remain viable and resist hydrolysis or other extraction mechanisms.**

relative scale of clay properties

Use this brief review of available clay types to help you decide which clay might best fit your needs.

CLAY TYPE LEGEND		
SC = soft clay	HC = hard clay	WW = water-washed
TWW = treated water-washed	CC = calcined clay	TCC = treated calcined clay

Best Compound Cost: SC > HC > WW > CC > TWW > TCC (SC > HC due to higher possible loadings even though SC is slightly higher cost per pound)

Reinforcement - Tensile and Modulus: TWW > WW, HC > TCC > CC, SC

Electrical Resistivity: TCC > CC > TWW > WW > HC, SC

Compression Set Resistance: TCC > CC > TWW > SC > WW > HC

A peroxide-cured EPDM was tested for compression set, 70 hrs/120°C, for comparison of various non-black filler types:

	C/S %
Treated calcined clay (TCC)	29
Calcined clay (CC)	32
Talc	49
35 m^2/gm silica	50

The calcined clays significantly enhance set resistance.

Color/Brightness: TCC, CC, TWW, special WW > WW > SC, sp HC > HC

Processability: TCC, CC > TWW, SC > WW > HC

While it seems every compounder is well aware of the usefulness of clay as a low-cost filler, it is important that a compounder not limit himself to the lowest common denominator. A wide variety of clays exist that can be fashioned into unique compounds with unusual processing parameters, good performance properties (some like electrical properties that are unmatched by any other filler), all at a reasonable cost. It will be advantageous for you to become familiar with the many clay types so you can pick the exact clay needed for special applications. And when in doubt, call the Akrochem Tech Service Dept. for help in choosing a clay.

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