

## SILICA AND SILICATES AS FILLERS IN RUBBER INDUSTRY

By

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Unfilled rubber compounds both natural and synthetic commonly termed gum vulcanizates are suitable for relatively few commercial applications. Fillers are used to modify a rubber compound to a consumer requirement. Of these, reinforcing fillers are known to increase hardness, stiffness, tensile strength and resistance to tear or abrasion of vulcanized rubber. Non-reinforcing fillers are used primarily to reduce cost, or to obtain a range of physical properties which will be satisfactory for an intended application. Such loading material could also be described as extenders or diluents. Such fillers may also be selected to impart certain desirable handling properties to a compound such as uncured dimensional stability in calendering, and extension. The term silica and silicates covers a wide range of white fillers both reinforcing and non-reinforcing, which are extensively used in the rubber industry.

A broad classification would separate these silicas and silicates into four classes, namely;

- (A) Pulverised naturally occurring materials
- (B) Precipitated, hydrated silicas and silicates
- (C) Anhydrous silicas and silicates produced by a thermal process and,
- (D) Aerogels

Group (A) includes;

- (i) Clays
- (ii) Talc
- (iii) Quartz
- (iv) Kieselguhr
- (v) Asbestine
- (vi) Mica
- (vii) Slate-flour
- (viii) Calcium silicate

Group (B) includes:

- (i) Hydrated aluminium silicate.
- (ii) Hydrated calcium silicates.
- (iii) Hydrated sodium silico-aluminate
- (vi) Hydrated magnesium silicate.
- (v) Hydrated silica

Group (C) includes:

- (i) Anhydrous magnesium silicate
- (ii) Anhydrous silica

Group (D) includes special types of anhydrous silica.

## Group (A) Fillers (naturally occurring)

### (i) Clays:

The term clay refers to a physical rather than a chemical composition and can be described as a system of hydrated aluminium silicate and varying amounts of lime, magnesia, sodium and potassium oxides. The most common rubber clays are predominantly kaolinic. Kaolin, Bentonite, china clay and seolex are examples of such different compositions of clay. Depending on the particle size, clay can be distinguished as 'hard and soft' (chemical composition is  $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$  in various ratios).

Clays are quite popular as low-cost fillers imparting high modulus and tensile strength and moderate abrasion-resistance. But the compounds may be slow-curing and yet be scorchy.

### (ii) Talc:

Talc is a hydrated magnesium silicate and is the softest coherent mineral known. In the rubber industry it is widely used as a dusting material and it also finds some use as an inert filler in articles such as flooring and electrical insulating compounds.

### (iii) Quartz:

This is common sand and is a crystalline form of silicon dioxide ( $\text{SiO}_2$ ). Ground quartz finds a limited use as an inert filler in acid resistant applications as ebonites and as an abrasive in eraser compounds.

### (iv) Kieselguhr:

This is commonly called diatomaceous earth and is a porous form of amorphous silica. The origin of this is the diatoms and other micro-organisms, the skeletons of which were deposited at the sea-bottom, millions of years ago. Kieselguhr has a rather large particle size and is non-reinforcing.

### (v) Asbestine:

Asbestine is a hydrated magnesium silicate which is primarily used as a low-cost filler.

### (vi) Mica:

Mica is naturally formed by the weathering of feldspar  $\text{K}_2\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O} - \text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  (Mica) (Feldspar)  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  (Kaolin) and others

Until comparatively recent times, mica was used mainly as a lubricant or a dusting material in the rubber industry. But lately mica has been used in latex-foam as a load-bearing filler along with clay where a filler like whiting would impair such properties. This characteristic is due to their plate-like structure.

### (vii) Slate-flour:

A hydrated magnesium silicate which finds very limited use as even a low cost filler due to large particle size.

### (viii) Calcium silicate:

Naturally occurring calcium silicate is quite sparingly used in the rubber industry due to its large particle size.

## Group (B) Fillers:

These fillers are manufactured using different methods of preparation based on different raw materials. But in general the process used involves melting of sand along with sodium carbonate and then fusing to give sodium silicate. This is reacted with an acid or metal salt solution, washed, filtered and dried. This is pulverised to give the hydrated silica or silicate. By replanting the acid with calcium or aluminium salts, the respective silicate could be obtained.

### (i) Hydrated aluminium silicate:

At present there are about a dozen different types of precipitated aluminium silicates in the market. The particle size is very fine and varies between 10 - 50 milli-microns and they are all alkaline with pH a range of 9 - 11.

Aluminium silicates are good reinforcing fillers and are used in all types of rubbers. They give comparatively harder vulcanizates than calcium silicates. They require a higher dosage of accelerators and would need booster additives like glycol or amine.

Sodium silico aluminate too imparts higher modulus, hardness and resilience to the compounds than calcium silicates.

### (ii) Hydrated magnesium silicates:

No materials of this category are available in the market for the rubber industry.

### (iii) Hydrated silicas:

This class embraces some of the most popular reinforcing white fillers. Their particle size could vary between 10 - 30 millimicrons and pH could be between 6 - 11.

In comparison with the silicates the hydrated silicas give stiffer, harder stocks and require special milling techniques when compounded with NR on the open mill if optimum properties are to be obtained. Special attention has to be paid in acceleration to even a greater extent than for silicates. When properly compounded they give properties on par with furnace blacks. Therefore it is important to adjust the accelerator content and essential to use an activator of the glycol or amine type.

In general the silica loaded vulcanizates show low modulus and high elongation which results in good flex - cracking resistance. This coupled with the high tensile and tear strength that the silica imparts, makes it a very useful filler.

Also, they are extensively used in applications where transparency or translucency are important factors, because of their very close refractive index to that of rubber.

## Group (C) Fillers:

### (i) Anhydrous magnesium silicate:

The only commercially available type is produced by an electrothermal process. Little information is available on this material and it is assumed that the properties are somewhat inferior to those of anhydrous silicas.

### (ii) Anhydrous silicas:

Usually, anhydrous silica or silicate is produced by a thermal or pyrogenic process either by rapid hydrolysis of diluted silicon tetrachloride vapours at high temperature or by burning ethyl silicate and collecting the product on a cold surface.

These products have a very fine particle size (0.015 - 0.020) which is finer than precipitated silicas. Because they are less agglomerated and cause greater hardening and stiffening they can not be easily mixed into rubber.

These fillers are sometimes referred to as 'white carbon blacks' and are at present being used for experimental production of coloured tyres.

**Group (D) Fillers:**

Aerogels are made by replacing the water in a silica-gel with an organic liquid to form an organogel. This is then heated in an autoclave and the organic liquid is thus removed without collapsing the gel. Such material is hardly produced in a commercial scale.