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# PRECIPITATED SILICA - CHARACTERISTICS AND ITS INFLUENCE IN RUBBER COMPOUNDS

Precipitated silica is produced by the Solution Process through the reaction of Alkalisilicate solutions with acid under controlled conditions, followed by precipitation. Precipitated Silica is considered as the semi-reinforcing white fillers and its structure is almost similar to that of the carbon black structure. Its particle size can range from 5 nm to 50 nm in diameter.



Transmission electron micrograph of precipitated silica showing aggregate structure



Unlike carbon black, which has similarly small primary particles, silica's "structure" is not permanent, Hydrogen bonding among the particles will form aggregates (three dimensional clusters) and range in size up to 500 nm in dia., and these aggregates may loosely bond as agglomerates. Compounding, however, disrupts agglomerates and even, to a certain extent, aggregates. So for example a compound with a 20nm average particle size silica can contain primary particles plus aggregates as large as 100 nm.

In compounds, ppt. silica is used to improve the tear strength, resistance to flex fatigue (cracking, cut-growth), heat ageing, stiffness, abrasion resistance and importantly Hot-tear resistance.



## **GENERAL CHARACTERISTICS OF PRECIPITATED SILICA**

Precipitated Silica	
	Range
BET Surface Area, m <sup>2</sup> /g	
Reinforcing	125-250 (10-40 nm)
Semi-reinforcing	35-100 (>40 nm)
Free Water, %@105°C	3-9
Bound Water, % (silanols)	2.5-3.5
pH	
Reinforcing	5-7
Semi-reinforcing	6-9
Salt Content, %	0.5-2.5
Specific Gravity in Rubber	1.95-2.05

The reinforcing properties of ppt. silica can usually be related to the particle size  $\rightarrow$  10-40 nm - particles are reinforcing, while 40+nm particls are semi reinforcing. i.e. the particles surface area of silica in the range of 125-250 m<sup>2</sup>/gm is generally reinforcing while in the range of 35 – 100 m<sup>2</sup>/gm are semi-reinforcing.

Influence of ppt. silica on the physical properties of a Rubber compound with 45 phr of silica:

Silica Surface Area, m²/g	60	150	185	220
Hardness	58	66	67	68
M300, MPa	4.0	3.6	3.0	3.1
Tensile, MPa	6.9	20.5	19.9	18.6
Trouser Tear, kN/m	3	27	36	49
Elongation, %	450	735	750	750
Abrasion Index	25	68	70	78

Here as the particle size surface area increases, the tear strength also increases, Its abrasion resistance is also get increased.



## **INFLUENCE OF THE SURFACE ACTIVITY & BOUND WATER CONTENT**



Ppt Silica is having the adsorbed free water and the its surface is saturated with silanol groups. This water acts as a Barrier and inhibits the reaction of accelerators and soluble zinc with the surface silanol groups. Depends on the % of the adsorbed water the curing cycle will also differ, as shown below.

<b>Precipitated Silica</b>		
Silica Free Water, %	3.8	0.7
MDR, 159°C, T <sub>90</sub> min.	17	30
Mooney Viscosity	57	112
Durometer	61	64
M300, MPa	2.3	3.0
Compression Set	69	77
PICO Abrasion Index	45	68

Low moisture ppt. silica is impractical to manufacture due to very high cost and also due to the natural tendency of the silica molecules to absorb moisture to maintain equilibrium with the relative humidity of its environment.

Hence this water content results in inconsistent or unexpected results in the compounds and end up in batch-to-batch variation as the water content in the compound is also varies due to varied water content during the mixing process.

To overcome this the surface of the silica has to be modified using the coupling agents like DEG, PEG, Siloxanes, Triethanol amine etc.



PEG 3350, phr	0	2	4
ODR, 144°C, Teo min	34	19	16
Viscosity, ML, 100	51	41	39
Hardness	59	66	60
Flexometer HBU, °C	32	29	22

#### Glycol is a more dependable buffer than water

High Molecular weight polyethylene glycol is used because of its low volatility, but DEG, Glycerine, Triethanolamine also used as well. These glycols/amines insulates the surface of the silica particle from reaction with accelerators and soluble zinc. Various Silanes are also used as coupling agents:

> HS-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si-(-O-CH<sub>3</sub>)<sub>3</sub> 3-Mercaptopropyltrimethoxysilane (A-189)

H<sub>2</sub>N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si-(-O-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub> 3-Aminopropyltriethoxysilane (A-1100)

[S-S-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>Si-(-O-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub> Bis(3-triethoxysilylpropyl)tetrasulfide (Si-69)

#### STRUCTURE OF SILANE COUPLING AGENTS



Silane coupling of polymer to silicate surface

#### **OTHER USES OF PPT. SILICA ARE:**

- Detergent, Sodium CMC: Anticaking Agent, Free Flowing Auxiliary, Moisture Absorber to lighten the Bulk Density & Whitening Aid.
- Salt, Spices, Potassium Chlorate, Pharm Feed, Dehydrated Foods, as Anticaking Agent to give free flowing characteristics, Coating Aid etc.
- Toothpaste: Thickening Agent mostly used by Gel toothpaste manufactures.
- Paints & Pigments: Flattening, Matting Agent, Thixotropic Agent, Extender of TiO2
- Pesticides / Choline Chloride: Carrier Agent
- Plastics: Antiblocking Agent used in Transparent Master Batches.



## **SELECTION GUIDE OF MANSIL PRECIPITATED SILICA GRADES**

S. No.	PHYSICO- CHEMICAL PROPERTIES	TEST METHOD	UNIT	MANSIL-130	MANSIL-160	MANSIL-175	MANSIL-190	MANSIL-210
1	Appearance	Visual		White, Spray dried powder				
2	Bulk Density	ISO 787/11	gm/li t	250 +/- 30	250 +/- 30	250 +/- 30	250 +/- 30	80 - 140
3	Moisture @ 105°C, (For 2 hrs. in oven)	ISO 787/2	%	6 (Max.)				
4	Ignition Loss at 1000°C, (for 2 hrs. in furnace)	ISO 3262/11	%	5 (Max.)	5 (Max.)	5 (Max.)	5 (Max.)	6 (Max.)
5	pH (5% Slurry)	ISO 787/9		6 - 7	6 - 7	6 - 7	6 – 7	6 - 8
6	Surface Area, (BET - Single - Point)	ISO 5794-1/D	m²/g m	120 - 150	150 - 170	170 - 190	190-210	190-210
7	SiO2 Content	ISO 3262/17	%	98.0 (Min.)				
8	Soluble Salts		%	2.0 (Max.)				
9	Iron Contents (As Fe +3)		Ppm	200 (Max.)				
10	DBP Absorption,		%	220 (Min.)	230 (Min.)	240 (Min.)	240 (Min.)	260 (Min.)

Please Note: "Mansil" is the brand name for the precipitated Silica being manufactured by M/s.Gujarat Multi Gas Base Chemicals Pvt. Ltd., Gujarat.

Ram Charan Company | "Century Towers", 46, Barnaby Road, Kilpauk, Chennai - 600 010 Tel : +44 - 4353 9040 / 41 / 42 Fax : +44 - 4330 7050 Email : all@ramcharan.org

**Mumbai** | 09821216311 mumbai@ramcharan.org

**Hosur** | 09443272475

hosur@ramcharan.org

Kolkatta | 09433346713 calcutta@ramcharan.org

Madurai | 09843044928 madurai@ramcharan.org Hyderabad | 09848208821 hyd@ramcharan.org

**Cochin** | 09847030708 cochin@ramcharan.org **Chennai** | 044 43539040 chennai@ramcharan.org

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**Bangalore** | 09980777298 bangalore@ramcharan.org