Nepheline syenite as the smart alternative to crystalline silica fillers in silicone elastomers

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Nepheline syenite is a silica deficient functional filler and additive widely employed in a variety of polymers, adhesives, coatings, inks and colorant applications. Micronized sizes are valued for purity of color, gloss control, antiblocking in polyolefin films and coatings, and ease of dispersion, with low viscosity build, abrasion and superior weather resistance. It is composed of three feldspathic minerals in close to equal proportions, including: albite ($Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$); microcline ($K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$); and nepheline ($Na_2O{\cdot}K_2O{\cdot}2Al_2O_3{\cdot}4SiO_2$). A schematic illustrating the mineralogy and chemistry is shown in Figure 1.

Nepheline syenite is a geologically common mineral deposit. Nepheline syenite is a plutonic igneous rock consisting mainly of nepheline, sodium and potassium feldspars. In appearance, as a light colored and coarse grain sized material, it shows similarities with granite, without containing any free silica (Ref. 1). Nepheline syenite main reserves are in Russia, Norway, Canada and Turkey. Nepheline syenite deposits are also detected as byproducts of some mining projects. Nepheline syenite's high Al_2O_3, Na_2O and K_2O content make it a material that can compete with feldspars in the glass and ceramic industries. More specifically, nepheline syenite is used as an active agent for the formation of a glassy phase in ceramics that enhances the physical strength of the final product. As for the glass industry, the high aluminum content of nepheline syenite acts as a booster in resistance to breaking, as well as thermal endurance and chemical durability (Ref. 1). It has also been found to be useful as a quartz or crystalline silica filler replacement across several industries, particularly in coatings, adhesives and sealants.

Geologically, the feldspathic combination known as nepheline syenite can only form in an Si deficient metamorphic environment as it is slowly cooled and crystalized. The SiO_2 contained in albite, microcline and nepheline noted in the chemical formula is not "free-silica," because the silicon and oxygen are combined with aluminum, as well as sodium/potassium, and no combinations of SiO_2 or quartz are detectable in the ore body. Feldspars, although alkali containing,

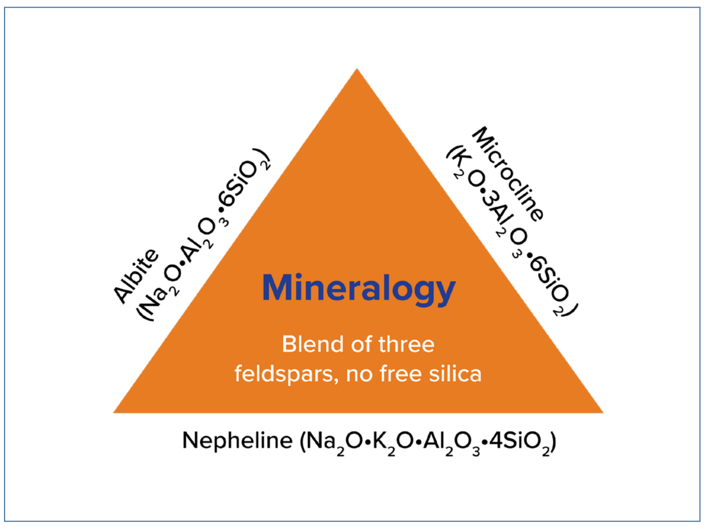

Figure 1. Mineralogy and chemistry of nepheline syenite.

are also considered highly insoluble and resistant to most acids and bases, since the alkalis are chemically bound; but unlike most feldspar deposits which contain high levels of free crystalline silica, nepheline syenite deposits contain none. Iron bearing minerals like biotite and epidote, or non-ferrous minerals like sodalite, analcime or muscovite, are considered impurities, and are often associated with nepheline syenite ore and the grain structure. Depending on how well these typical impurities can be removed through industrial processing determines the color, purity and performance of the product.

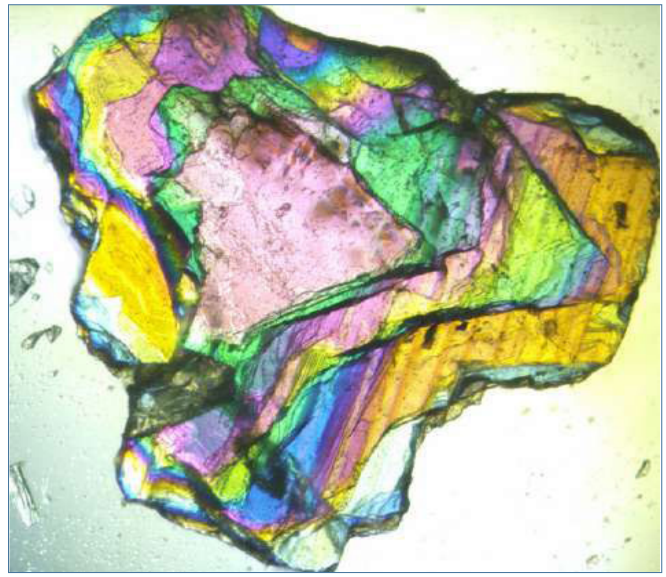

Figure 3. Photomicrographs courtesy of Dr. Gary Greenberg, www.sandgrains.com.

One of the largest, higher whiteness and more chemically consistent deposits is found in The Blue Mountains, Ontario, Canada. Beneficiated material from this location will be the primary material discussed in this article, along with its properties and its growing application in silicone elastomers. Photomicrographs of typical Blue Mountain nepheline syenite grains liberated from the ore and utilizing unique transmitted and reflected illuminations and transmitted polarized light microscopy techniques are provided in Figures 2 and 3, respectively. The photomicrographs reveal the grain shapes and transparency, and the polarized light image highlights the three feldspars and mineral interfaces found within nepheline syenite grains using these techniques (Ref. 2).

Figure 2. Reflected and transmitted illumination photomicrograph of liberated nepheline syenite grains from the ore.

Although it is deficient in crystalline silica, nepheline syenite (NS) otherwise provides physical performance properties which mirror ground crystalline silica (GCS) and microcrystalline silica (MCS) extenders commonly used in silicone elastomers. Since nepheline syenite functional fillers are naturally derived, and deficient in free silica and heavy or transition metals, they are typically less burdened by regulatory requirements such as REACH, OSHA, RoHS and TSCA. The micronized nepheline syenite fillers discussed here, from the Blue Mountain deposit, are also FDA generally recognized as safe (GRAS) for indirect food contact in polymer applications up to 50% by weight (Ref. 3).

Comparison of nepheline syenite properties with ground crystalline and microcrystalline silica

Figure 4 compares the typical particles and shapes of ground NS, GCS and MCS extenders. NS filler particle shapes are angular to blocky, and are more similar in particle morphology to GCS than MCS, which is more nodular or irregular as an alpha quartz with a finer specific grain size (since it is more weathered in nature).

Table 1 lists the typical properties of NS extenders in comparison with GCS and MCS. NS and GCS have similarly low oil absorption and surface area. Mohs hardness on the 1 to 10 scale is about 6 for NS; slightly less hard than GCS and MCS. NS is typically found to be less abrasive to compounding and processing equipment based on this property. The NS particles themselves are moderately hard, non-porous and possess high compressive strength, providing effective abrasion resistance in the polymer matrix. The low surface area and alkali aluminosilicate surface chemistry contribute to the ease of wetting, rapid dispersion and high loading, with low viscosity build. The NS surface chemistry also has abundant silanol (i.e., Si-OH) or surface hydroxy (-OH) groups available, as do most silica and silicates minerals, for effective use of coupling agents commonly used with silicone polymer chemistry. Optically, NS powders are more color neutral with a lower refractive index (RI) of 1.51 to 1.52, versus 1.55 for conventional GCS and MCS fillers. NS is also whiter and brighter, or less yellow, than GCS and MCS powders, and can yield cleaner, brighter colors, or transparency when desired.

Property	GCS	NS	MCS
Shape	angular	angular/ blocky	nodular
Mohs hardness	7	6.0 - 6.5	6.5
Refractive index (RI)	1.55	1.52	1.55
BET surface area (m^2/g)	2 - 7	2 - 7	5 - 8
GE brightness	88	92	86
Specific resistance ($\Omega cm*10^{-3}$)	26	23	25.7
Thermal conductivity (W/m*K) at 100°C	6	3	5
% moisture	0.1 - 0.3	0.1 - 0.3	0.1 - 0.3
Specific gravity (g/cc)	2.65	2.61	2.65

Table 1. Comparison of typical properties of nepheline syenite (NS) fillers with ground crystalline (GCS) and microcrystalline silica (MCS) fillers.

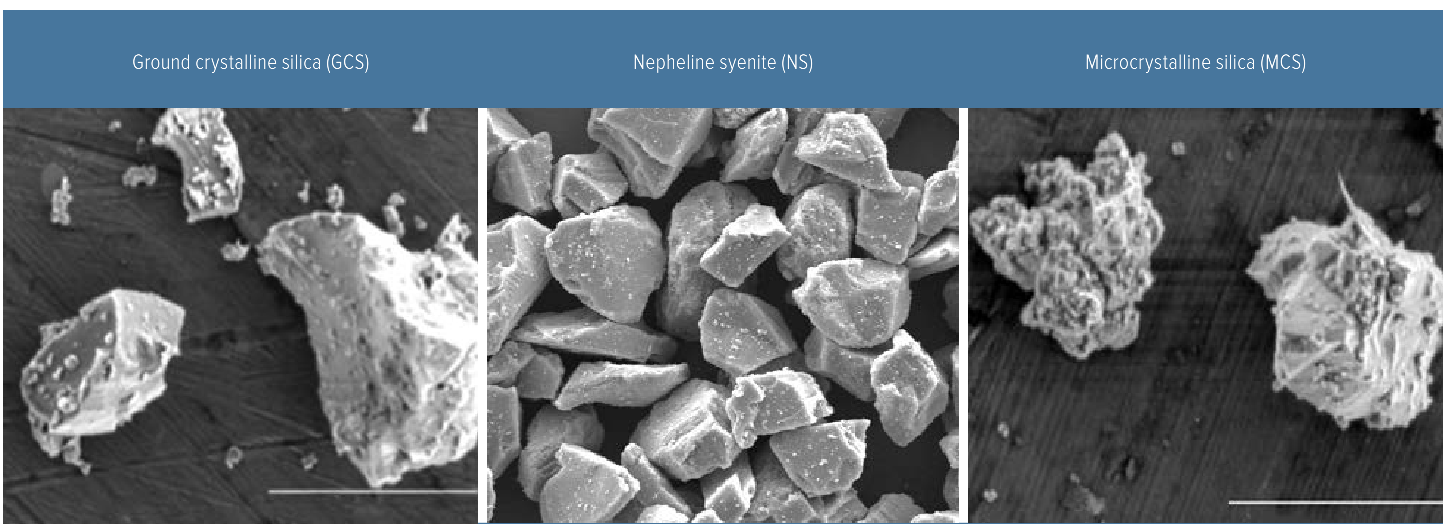

Figure 4. SEM photomicrographs comparing particle shape and morphology of micronized durable mineral fillers used in silicone elastomers.

The pH of NS, like all feldspathic minerals, is alkaline, in the 9.5 to 10.3 range, and higher than that of MCS and GCS, which are both slightly on the acidic side. The pH of NS can also be useful to assist with silicone rubber cure rates and/or coupling with functional silanes. In dielectric elastomer applications like insulative wiring, spark plug boot and jacket insulators, NS specific resistance properties are in line with GCS and MCS; and all three are very good insulators. GCS and MCS are also known to have good thermal conductivity properties, which are becoming more important for thermal management applications. NS, being feldspathic in nature, has lower thermal conductivity (K) at ambient temperature, but is on the same order as quartz based fillers. Unlike quartz, where K decreases with the rising temperature, NS or feldspathic minerals are less affected by rising temperatures (Ref. 4). And higher temperatures are common in many silicone applications. The Blue Mountain NS extenders are also low in other impurities like sulfur, for example; so it is believed to be more consistent in platinum catalyzed silicone elastomers by industry experts.

A comparison of specific properties for NS and GCS for filler sizes commonly utilized as silicone elastomer extenders is provided in Table 2. NS 15 and GCS 15 extenders with top sizes of 15 micron (i.e., D98 < 15 µm) and NS 10 and GCS 10 (D98 < 10 µm) are the most common sizes used in elastomers. The data were collected from published technical data sheets or inhouse testing. The higher brightness and pH associated with NS has already been discussed. Median particle size and reported oil absorption for equivalent grades are also relatively similar.

Silicone extender	Median particle size (µm)	Top size (D98 < %µm)	% > +325 mesh	pH	GE brightness	% Oil absorption
NS 30	6.8	30	0.1	10	87	26
GCS 30	5.5	30	0.1	6.5	84	29
NS 15	3.6	15	0.01	10	90	31
GCS 15	3.0	15	0.01	6.5	86	39
NS 10	2.5	10	0	10	92	33
GCS 10	2.0	10	0	6.5	86	39
NS 5	1.7	6	0	10	94	40
GCS 5	1.3	5	0	6.5	88	35

Table 2. Comparison of extender properties of standard nepheline syenite fillers with a standard size of ground crystalline silica fillers used in silicone elastomers.

Applications of nepheline syenite and introduction timeline in silicone elastomers

The full benefits of nepheline syenite have not been unveiled fully in silicone elastomers until more recently. NS has been used in silicone elastomers for over two decades, and probably longer. The spark that lit the fire was IARC's (International Agency for Research on Cancer) reclassification of crystalline silica from a class II to a known class I hazardous material in 1997 (Ref. 5). Some leading automotive manufacturers had restrictions on IARC class I materials, and some OEM automotive silicone elastomer suppliers took notice. The NS 10 size was trialed as a direct offset in silicone rubber OEM automotive exhaust connectors to GCS 10 in 2000, with identical performance reported, and is still used in this application today.

A generalized timeline for the introduction of NS fillers in silicone applications is provided in Figure 5. Current uses of micronized NS in silicone polymers and elastomers also include spark plug wire and boots, wire and cable insulators, consumer durables, gaskets, o-rings, RTV adhesives, sealants and elastomeric roof coatings. It is estimated up to 20% of silicone elastomer materials traditionally filled with GCS or MCS are now using NS fillers in the North American silicone rubber market. This trend is expected to continue, with OSHA lowering the silica dust exposure limit again in 2016 (Ref. 6), and new performance data validating plentiful anecdotal customer feedback about higher tensile with cleaner colors. Plus, NS is a natural filler and can improve the Environmental, Social and Governance (ESG) profile of silicone elastomers; and some previously unfilled elastomer applications are considering NS for cost reduction, but also for improving the ESG profiles.

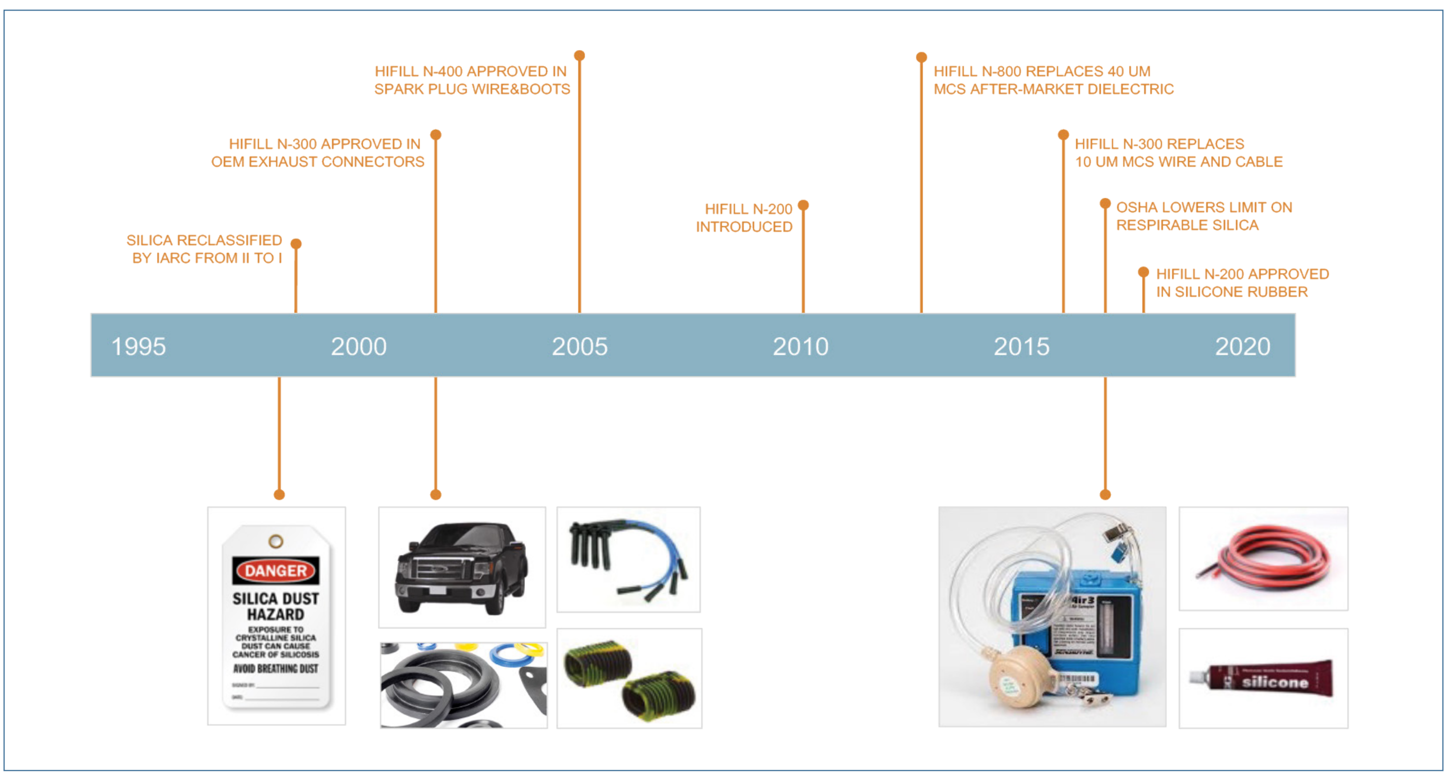

Figure 5. Timeline for the introduction of NS in silicone systems over the past two decades.

Experimental

Although plenty of anecdotal feedback on the performance of NS in silicone rubber was discussed in the industry for years, very little published or shared data have been available. Recently, standard grades of NS 15 and GCS 15 were compared in standard and commercial silicone elastomer sheet molding compounds. The two basic formulas considered are found in Tables 3 and 4. GCS 15 and NS 15 extenders were considered at equal loading of 50 phr at two durometer levels, and were prepared on a commercial compounding line. The sheet molding compounds with the two different extenders were sent to an accredited third party laboratory and compared in blind testing in accordance with ASTM AA-59588B.

60 DUROMETER SHEET MOLDING COMPOUND	
Ingredient	**Parts**
60 durometer hardness silicone base	100
DBPH-50 catalyst	1.0
Extender	50.0

Table 3. Commercial silicone sheet molding compound used for comparative testing of equivalently sized GCS 15 and NS 15 extenders in a 60 durometer silicone elastomer.

70 DUROMETER SHEET MOLDING COMPOUND	
Ingredient	**Parts**
70 durometer hardness silicone base	100
DBPH-50 catalyst	1.0
Extender	50.0

Table 4. Commercial silicone sheet molding compound used for comparative testing of equivalently sized GCS 15 and NS 15 extenders in a 70 durometer silicone elastomer.

60 DUROMETER SHEET MOLDING COMPOUND				
Specification	**AA-59588B Test**	**GCS 15**	**NS 15**	**Limits**
ASTM method	Appearance	Pass	Pass	Pass / Fail
D792	SG (g/cc)	1.427	1.429	Report
2240	Durometer (A)	511	56	55 to 65
D412	Tensile (psi)	801	850	650 minimum
D412	Elongation (%)	343	294	100 minimum
D412	Modulus 100%	342	394	Report
D624	Tear strength, PPI die B	93	90	Report
D395 method B, 70 hours at 150°C	Compression set (%)	11.70	13.8	25 maximum
D573, 70 hours at 225°C	Dry heat resistance			
	Change in hardness (points)	+6.4	+2.7	+10 maximum
	Change in tensile (%)	+3.1	+1.2	-20 maximum
	Change in elongation (%)	-40.9	-26.5	-40 maximum
D2137 at -62.2°C	Low temperature resistance			
	Brittleness	Pass	Pass	Pass / Fail
D471 70 hours at 100°C	Water immersion			
	Volume change	-0.75	-0.41	+5 maximum

Table 5. Comparison of standard sized nepheline syenite and ground crystalline silica extenders in 60 durometer sheet molding compounds in accordance with ASTM AA-59588B.

Results and discussion

The results for the side by side testing of NS 15 and GCS 15 in 60 and 70 durometer silicone base formulas are reported in Tables 5 and 6, respectively. In the 60 durometer system, specific gravity was similar. Generally, NS (2.61 g/cc) will provide slightly lower density than GCS (2.65 g/cc). Oddly, GCS 15 durometer hardness was below the desired target, even though it is normally utilized in the commercial formula; while NS 15 met the specification. NS 15 measured higher for tensile strength, which is what is consistently reported with NS fillers. Both materials easily met elongation and modulus targets. Tear was similar. GCS 15 was slightly better for compression set; but NS 15 was better for dry heat aging tests, where GCS 15 was borderline passing for percent elongation.

In the 70 durometer formula, both NS 15 and GCS 15 easily met all the requirements, except for heat aging. GCS 15 was not as consistent for heat aged physical properties as was NS 15. NS 15 was again better for tensile properties, while compression set was identical.

70 DUROMETER SHEET MOLDING COMPOUND				
Specification	AA-59588B Test	GCS 15	NS 15	Limits
ASTM method	Appearance	Pass	Pass	Pass / Fail
D792	SG (g/cc)	1.42	1.41	Report
2240	Durometer (A)	67	68	65 to 75
D412	Tensile (psi)	860	894	650 minimum
D412	Elongation (%)	352	340	80 minimum
D412	Modulus 100%	442	486	Report
D624	Tear strength, PPI die B	116	112	Report
D395 method B, 70 hours at 150°C	Compression set (%)	13.4	13.1	25 maximum
D573, 70 hours at 225°C	Dry heat resistance			
	Change in hardness (points)			+10 maximum
	Change in tensile (%)			-20 maximum
	Change in elongation (%)			-40 maximum
D2137 at -62.2°C	Low temperature resistance			
	Brittleness	Pass	Pass	Pass / Fail
D471 70 hours at 100°C	Water immersion			
	Volume change	-0.32	0.0	+5 maximum

Table 6. Comparison of standard sized nepheline syenite and ground crystalline silica extenders in 70 durometer sheet molding compounds in accordance with ASTM AA-59588B.

Conclusion

Nepheline syenite is a versatile and unique durable extender, possessing properties that are useful in a wide range of filled elastomers applications. It has desirable industrial hygiene advantages over conventional ground silica options, with similar physicals and typically higher tensile strength with good dielectric and thermal conductivity properties to meet future silicone formulators extender needs. Nepheline syenite is not new to the elastomer industry, with use in demanding applications going back over three decades. What is new are the performance benefits of nepheline syenite in elastomers and filled polymer systems, which are being more fully explored.

Future work will consider the chemical purity properties of nepheline syenite extenders for reliability in platinum catalyzed systems; and expanded applications testing with existing and new grades. The finer top size for improved physicals will provide ultra low abrasion properties ideally suited for extrusion and injection molding applications that can be sensitive to process wear (that often go unfilled, but could be with the right material solutions).

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