

HAZARDS IN FILLER USE

Most fillers used today are not hazardous materials but some are, those require special handling and processing to reduce the potential hazard. Table 20.1 gives an overview of properties of fillers which help in the determination of safe handling practices.

Table 20.1. The properties of fillers

Name	CAS #	Health**	Flammability**	Reactivity**	Contact**	Storage color code***	Toxicity LDLO, mg/kg	Carcinogenicity	TWA, mg/m ³	Silicosis
Aluminum	7429-90-5	1	4	2	1	red		no	10	
Aluminum hydroxide	21645-51-2	1	0	0	1	orange	150	no		
Aluminum oxide	1344-28-1	1	0	0	1	orange	90	no	10	
Aluminum silicate	1302-76-7						90		2	
Ammonium phosphate	7783-28-0	1	0	1	1	orange		no	2	
Anthracite	120-12-7	1	1	0	1	orange	430	no		
Antimony pentoxide	1314-60-9						4000		0.5	
Antimony trioxide	1309-64-4	3	0	0	2	blue	3250	no	0.5	
Asbestos	12001-29-5						300	yes	0.2*	
Ash, coal		1	0	0	1	orange				yes*
Ash, fly						orange		no	10	
Barium sulfate	7727-43-7	1	0	0	0	orange		no	10	
Bauxite	1344-28-1							no	10	
Bentonite	1302-78-9						1200			
Beryllium oxide	1304-56-9	3	1	0		red			0.002	
Boron	7440-42-8		4				310			
Calcite	471-34-1	0	0	0	1	orange		no	10	yes
Calcium aluminate	12042-68-1	1	1	0		orange				
Calcium borate	12007-56-6	2								

Name	CAS #	Health**	Flammability**	Reactivity**	Contact**	Storage color code***	Toxicity LDLO, mg/kg	Carcinogenicity	TWA, mg/m³	Silicosis
Calcium carbonate	471-34-1	0	0	0	1	orange		no	10	yes*
Calcium hydroxide	1305-62-0	1	0	1	2	orange	7340	no	5	
Calcium silicate	1344-95-2								10	
Calcium sulfate anh.	7778-18-9	1	0	0	1	orange		no		
Carbon black	1333-86-4	1	0	0	1	orange		no	3.5	
Clay		1	0	0	0	orange				yes*
Copper spheres	7440-50-8	0	0	0	1	orange		no	1	
Crystobalite	14464-46-1								0.05	yes
Dawsonite	12011-76-6						200			
Diatomaceous earth	61790-53-2							no	10	yes*
Dolomite	471-34-1	0	0	0	1	orange		no	10	yes
Ferrite		0	0	0	0	orange				
Glass fibers		1	0	0	1	orange		no	10	
Gold	7440-57-5						58			
Graphite	7782-42-5								2	yes*
Iron	7439-89-6	1	3	1	0	red	20	no		
Kaolin	1332-58-7	0	0	0	1	orange		no	10	
Lead	7439-92-1		3				160		0.15	
Limestone	471-34-1	0	0	0	1	orange		no	10	yes
Lithium aluminum silicate	1302-66-5								5	
Lithopone	1345-05-7	2								
Magnesium aluminum silicate	12174-11-7								10	yes*
Magnesium carbonate	23389-33-5	1	0	1	0	orange		no		
Magnesium hydroxide	1309-42-8	1	0	0	1	orange		no		
Magnesium oxide	1309-48-4	1	0	1	1	orange		no	10	
Marble	471-34-1	0	0	0	1	orange		no	10	
Mica, muscovite	12001-26-2	1	0	0	1	orange			3	yes*
Molybdenum	7439-98-7		3				125		10	
Molybdenum disulfide	1317-33-5									
Montmorillonite	98901-77-4							no		
Nickel	7440-02-0							yes	0.05	
Palladium	7440-05-3		3							

Name	CAS #	Health**	Flammability**	Reactivity**	Contact**	Storage color code***	Toxicity LDLO, mg/kg	Carcinogenicity	TWA, mg/m ³	Silicosis
Perlite	93763-70-3	1	0	0	1	orange		10	yes*	
Pyrophyllite								0.14		
Ruthenium dioxide	12036-10-1									
Silica, fumed	69013-64-2							0.2	no	
Silica, fused	60676-86-0							0.1		
Silica, hydrated	7631-86-9							10		
Silica, precipitated	1343-98-2	1	0	0	1	orange	no	10		
Silica, quartz	14808-60-7							0.1	yes	
Silica, sand	7631-86-9	1	0	0	1	orange		80		
Silica, gel	1343-98-2	1	0	0	1	orange	no	10		
Silver	7440-22-4							0.1		
Smectite	12199-37-0							2	yes*	
Sodium aluminum silicate	1344-00-9	1	0	0	0	orange				
Soot		1	2	0	0	orange	yes			
Starch	9005-25-8	1	2	0	0	orange		15		
Syenite	37244-96-5							10	no	
Talc	14807-96-6	1	0	0	1	orange	no*	2		
Titanium boride	12045-63-5	1	0	0	0	orange				
Titanium dioxide	13463-67-7	0	0	0	1	orange	no	10		
Tungsten	7440-33-7		4			red		5		
Vermiculite	1318-00-9	1	0	0	1	orange	no	10		
Wood flour	9004-34-6							10		
Wollastonite	13983-17-0	1	0	0	0	orange	no			
Zeolite	1344-00-9	1	0	1	1	orange				
Zinc borate	1332-07-6									
Zinc oxide	1314-13-2	2	0	0	0	orange	630	no	5	
Zinc sulfide	1314-98-3									
Zirconium oxide	1314-23-4	1	0	0	1	orange		5		
Zirconium silicate	14940-68-2							5		

*in carcinogenicity means - if contains asbestos; in silicosis risk means - if contains crystalline silica; in TWA means - fibers per cm³.

**the following rating is used: 0 - no hazard, 1 - slight, 2 - moderate, 3 - severe, 4 - extreme hazard

***storage area is chosen as follows: orange - general, blue - special, red - hazardous

Several fillers, including asbestos, nickel, and soot, are carcinogens. The health risk due to asbestos exposure is well documented.¹ Exposure to asbestos increases the risk of lung cancer, mesothelioma, asbestosis, pleural thickening, and gastrointestinal cancer. The first four diseases are caused by inhalation of asbestiform fibers, whereas the last is caused by ingestion.

The worst lung damage is caused by asbestos fibers which reach the lower parts of the respiratory tract. Fiber length is also a factor. The fibers longer than 3 μm are the most dangerous. No difference was found¹ between various forms of asbestos. The report¹ also considers other types of fibrous materials both natural and man-made, such as attapulgite, erionite, fibrous glass, mineral wool, and ceramic fiber. These fibers also fulfill the size criteria (diameter, length), with the exception, perhaps, of attapulgite, the fibers of which are generally shorter than 1 μm.

People of central Turkey who live in an area rich in erionite frequently suffer from lung cancer and mesothelioma. It is not yet known definitely, if the risk of cancer from exposure to other fibrous materials is considerably lower than that of exposure to asbestos. But the existing data seems to show that the risk of health problems, due to exposure to fibers other than asbestos is less.

Table 20.2 summarizes the data on the effect of asbestos exposure on the death rate caused by various asbestos-related diseases.

Table 20.2. Mortality data for asbestos related diseases¹

Occupation	# exposed	Total death	Mesothelioma	Respiratory cancer	Gastrointestinal cancer
Mining & milling	14,332	4,711	37	372	312
Manufacturing	20,474	3,110	95	547	284
Insulation	18,594	2,871	226	557	150
Shipyards	8,416	3,013	31	211	147

These data link asbestos to various forms of cancer. In the last several years, industry has made a big effort to eliminate asbestos from numerous products and asbestos is no longer an active factor.

Some types of talc contain high concentrations of tremolite. Tremolite has two varieties: asbestiform and nonasbestiform. Asbestiform may cause tumors in humans similar to various other forms of asbestos. The nonasbestiform tremolite was recently studied by a group of experts who reviewed previous studies and conducted its own experiments.^{2,3} Nonasbestiform tremolite contained in New York state talcs did not produce a carcinogenic response in test animals. It has morphological features different from asbestiform.^{2,3} Since talc is commonly used in cosmetic powders these studies are needed to protect the general public from exposure and also prevent the exclusion of materials on any basis other than scientific evaluation. But studies of pharmaceutical talc revealed that some of these talcs contained about 200,000 fibers longer than 5 μm in 1 mg of their mass.⁴ A continuing evaluation is needed to segregate safe mineral forms from the dangerous asbestiform variety.

Fillers containing crystalline silica pose dangers. In Table 20.1, there are fourteen groups of fillers which contain some quantities of crystalline silica. In the United States, about 1 million workers are exposed to crystalline silica of these 250 will die from silicosis. The group most exposed are construction workers who use materials containing crystalline silica for sandblasting. The plastics industry was not in the top 10 list of industries but the potential danger in the plastics industry should be understood since the risk can be eliminated with proper protection. Chronic silicosis occurs after 10 or more years of overexposure.⁵ But accelerated silicosis from higher exposures can develop in a shorter period of time (5-10 years). The action of crystalline silica on the lungs results in the development of a diffuse, nodular fibrosis involving the parenchyma and the lymphatic system. Fibrosis increases for several years after contact is terminated. Typical complications include cardiac failure and tuberculosis. Fillers containing crystalline silica are included by IRAC in Group 3 which contains materials for which there is insufficient evidence of causing cancer. All fillers which contain more than 0.1% crystalline silica require a warning in MSDS and on the product label.

Various industries use large quantities of fumed and precipitated silica (amorphous silica). These forms of silica do not cause silicosis but protection from exposure to dust must be provided because any excessive dust decreases efficiency of lungs.⁶⁻⁸

Other than these, the fillers discussed in this book do not pose special dangers under their normal conditions of use other than when they are accidentally exposed to high temperatures. In such a situation, sulfates decompose, emitting toxic fumes; lithopone emits highly toxic fumes containing sulfur oxides and H₂S; antimony and zinc oxides emit toxic metal and zinc oxide, respectively.

Thus, with the exception of fibrous fillers, most fillers are relatively harmless materials, although they must be used with reasonable care.

Now information has been developed for carbon black.⁹⁻¹¹ International Agency for Research on Cancer changed the classification of carbon black from Group 3 to Group 2 (possible carcinogen). This was based on a study on rats. This caused one manufacturer, Degussa, to release results of medical studies on 677 employees indicating that carbon black could not be linked to cancer. The results of studies in the USA (2500 workers) and in the UK (1422) came to the same conclusions.¹⁰ How can this conflicting data be assessed? Recent changes in the implementation of new regulations have emphasized cooperation between industry and regulatory agencies.

These new cooperation efforts seem to be effective.¹¹ A commissioned study was carried out by the University of Birmingham to evaluate occupational exposure to carbon black. The study was conducted in 1987 and again in 1992. During the second study it was discovered that the exposure of workers was reduced by one half compared with the first study. The data from the first study led to the voluntary changes which gave the excellent results.

The potential for dust to explode is the other significant hazard of filler use. Particle size, concentration of particles, and strength of the source of ignition are important criteria for evaluating hazard. Of course, the material forming the dust must also be combustible. Smaller particles are easier to ignite because they have a larger exposed surface area available for ignition and combustion. The lower explosive limit depends on particle size. Also, smaller particles can accumulate greater electrical charges. The lower explosive limit is usually the factor of control. The upper limits are not established. The most violent

explosions occur when the amount of available oxygen matches the amount required for complete oxidation of the particulate. The data included in the Table 20.1 shows that metal particulates are the most hazardous explosive dusts. Carbon black is also a hazardous material in this respect. The explosibility index and the ignition sensitivity of carbon blacks is much lower than 0.1.⁹ Carbon black presents more of a fire hazard than a dust explosion hazard. None of the 19 samples tested was ignited by an electric spark source.⁹ Ignition temperature in air ranges from 445 to 890°C, and in oxygen, from 320 to 450°C. The concentration of oxygen required for ignition was in the range of 35 to 74 percent. The explosibility index of carbon black rose to more than 10 (several orders of magnitude) when carbon black was in a mixture with polystyrene and dioctyl phthalate. Such an increase indicates that mixtures of carbon black with other materials might be even more hazardous.

The moisture level of the particulate increases its ignition temperature. Also, the presence of an inert solid reduces its combustibility. Some particulates (limestone) are used to extinguish fires but mixtures of particulates may increase the explosion hazard. One simple method of reducing explosion hazard is to use an atmosphere of inert gas in processing and transportation. A dust cloud can be ignited by any conventional source but friction sparks, hot surfaces, the heat of friction, and static sparks are the most common sources of ignition.

Another potential hazard in using fillers is the possible formation of toxic materials. Twelve samples of silica fillers were studied with respect to their effect on the formation of N-nitrosamines in rubber compounds.¹² Figures 20.1 and 20.2 provide these data. Filler absorption of NO_x increases as the filler's specific surface area increases. This absorbed NO_x was found to react with amines in rubber and to produce N-nitrosamines. Greater absorption

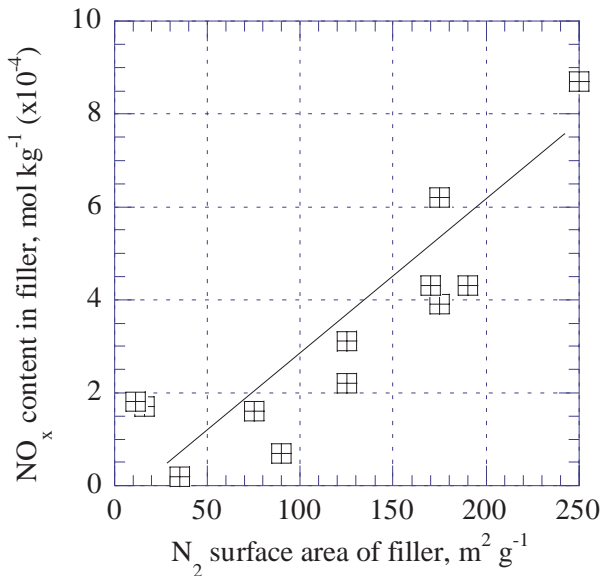


Figure 20.1. NO_x content vs. filler surface area. [Adapted, by permission, from Gorl U, De Kok J J, Bomal Y, Cochet P, Mueller H, *Kaut. u. Gummi Kunst.*, 47, No.6, June 1994, 430-4.]

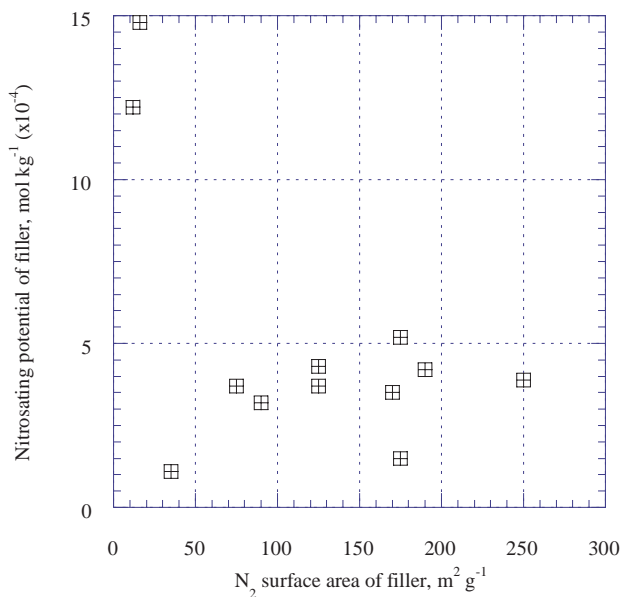


Figure 20.2. Nitrosating potential as a function of filler surface area. [Adapted, by permission, from Gorl U, De Kok J J, Bomal Y, Cochet P, Mueller H, *Kaut. u. Gummi Kunst.*, **47**, No.6, June 1994, 430-4.]

of NO_x did not cause an increase in the formation of nitrosamines. This may be explained by the fact that a precursor is trapped in the porous structure of silica and retained because of its higher chemical activity.

REFERENCES

- 1 **Asbestiform Fibers.** Non-occupational Health Risks. *National Academy Press*, Washington, D.C., 1984.
- 2 Roedelsperger K, Lojewski G H, Brueckel B, Weitowitz H J, *Staub-Reinhalt. Luft*, **44** (2), 62 (1984).
- 3 **The asbestiform and nonasbestiform mineral growth habit and the relationship to cancer studies.** Report. America Mining Congress and National Stone Association.
- 4 Wylie A G, Skinner H C W, Marsh J, Snyder H, Garzone C, Hodgkinson D, Winters R, Mossman B T, *Toxicology Appl. Pharmacology*, 147, 1997.
- 5 Sax N I, **Dangerous Properties of Industrial Materials.** *Van Nostrand Reinhold Co.*, New York, 1990.
- 6 **Hi-Sil Dust Exposure and OSHA Regulations,** *PPG Industries*, Pittsburgh, 1976.
- 7 **Aerosil. Fumed Silica.** *Degussa*, Frankfurt.
- 8 **Cab-O-Sil. Properties and Functions.** *Cabot Corp.*, Tuscola, 1985.
- 9 Nagy J, Dorsett H G, Cooper A R, *US Dept. of the Interior, Bureau of Mines*, TN23.U7, no. 6597.
- 10 *Eur. Rubb. J.*, **178**, No.8, 1996, 26.
- 11 Gardiner K, Calvert I A, van Tongeren M J A, Harrington J M, *Ann. Occup. Hyg.*, **40**, No.1, 1996, 65-77.
- 12 Gorl U, De Kok J J, Bomal Y, Cochet P, Mueller H, *Kaut. u. Gummi Kunst.*, **47**, No.6, June 1994, 430-4.