This invention relates to novel inorganic silicon and oxygen containing pigments. More specifically, this invention relates to fibrous inorganic compositions of silicon and oxygen which are especially useful as intermediates for making reinforcing pigments for elastomers and to methods for making the same.

"Monox" or solid, particulate, disproporitionated silicon monoxide (SiO$_2$) or (SiO$_2$)$_x$ where x and y are integers, is produced by the reaction of carbon and silica at high temperatures under reducing conditions, such as in an arc furnace, and allowing the gaseous reaction products containing SiO to condense in a partial or in an essentially complete vacuum or vacuum chamber or in an inert atmosphere or gas of nitrogen, argon, helium, CO, etc. In place of carbon, silicon or silicon carbide can be used to produce SiO gas. Alternatively, silicon metal can be cooled to SiO gas which then can be condensed. Still other methods for making "Monox" can be used.

Monox is characterized as being solid, finely-divided or particulate and exhibiting under the electron microscope a mixture of fibrous particles and non-fibrous and possibly spherical particles. If the process is conducted in a manner that the inert condensing gas and the silicon monoxide gas stream mix together with little or no turbulence, especially long and tendrilorous fibers are obtained. Moreover, the amount of the non-fibrous particles is materially reduced and is less than the fibrous particles. In such processes the inert condensing gas also should be essentially pure, that is, it should contain only a few parts of an oxidizing gas per million parts of condensing gas, or if it is of a commercial variety containing a minor amount of oxygen or oxidizing gases, it should also contain a minor amount of an anion such as ammonia, ethyl amine and the like or a hydrogen-furnishing gas such as hydrogen, methane, ethane, etc. to remove any traces of oxidizing gas in the inert condensing gas as well as in the furnace gases. If desired, generally non-fibrous Monox can be obtained by merely blowing the silicon monoxide gas stream from the furnace with any of the above inert condensing gases, or gas mixtures, to cause turbulence in the mixing gas streams. The Monox may contain minor amounts of nitrogen, usually about 1-8% by weight of bound nitrogen probably as (SiONH)$_2$, x being an integer, i.e.

\[
\begin{align*}
\text{O} & \quad \text{H} \\
\text{N} & \quad \text{Si}
\end{align*}
\]

in which nitrogen is attached to two silicon atoms, so that part of the Si is tied up if the inert condensing gas was nitrogen and if it also contained from about 0.5 to 9% by volume of a gaseous amine. However, very little (less than 1% by weight) or no nitrogen is present in Monox if a pure inert condensing gas is used or a commercial variety of inert gas containing a hydrogen furnishing gas is used and the silica and carbon used are very pure. The latter described Monox effects a less rapid cure in rubber containing compositions due to its greater acidity.

In general, the fibers of the fibrous type of Monox have a ratio of length to width of from about 10:1 to 50:1 or greater and exhibit a surface area of from about 60 to 200 square meters per gram although the surface area may be smaller or larger. Their average length will vary from about 50 to 600 millimicrons or higher. The non-fibrous particles, if any, in the mixture may have an average particle size of from about 5 to 200 μ and a surface area of from about 200 to 300 square meters per gram. When the SiO gas is blown with an inert gas, the generally non-fibrous particles obtained have a random range of particle sizes of from about 5 to 200 μ and a surface area of from about 200 to 300 μ²/³.

It has been found that "Monox," particularly where the fibers are in a major amount and very long and the ratio of the length to the width of the fibers is high, is useful as a reinforcing pigment for various elastomeric products such as rubber, vinyls, polyuretheranhes, silicones, and the like. However, Monox is brown and, accordingly, the color of products to which about are brown. This color can not be masked by the use of color pigments without materially destroying the reinforcing properties imparted by the Monox.

It, thus, would be highly desirable to provide a method for producing a Monox type pigment, especially in the fibrous form, which is light to white in color so that when compounded with elastomeric compositions it would produce light colored to white products, would not adversely affect the color of the elastomer itself, and could be compounded with relatively minor amounts of pigments, dyes, etc., to provide useful, reinforced, colored, elastomeric products. Accordingly, it is a primary object of the present invention to provide a method for making a light colored to white, solid, particulate composition from disproporitionated silicon monoxide.

It is another object of this invention to provide a light colored to white, solid particulate composition obtained from disproporitionated silicon monoxide.

Another object is to provide a method for producing a composition from disproporitionated silicon monoxide which is white, solid, particulate and substantially fibrous.

Yet another object is to provide a composition of matter from disproporitionated silicon monoxide which is white, solid, particulate and substantially fibrous and is useful as a reinforcing pigment for elastomers.

These and other objects and advantages of the present invention will become more apparent to those skilled in the art from the following detailed description and examples.

According to the present invention, it has been discovered that brown "Monox" prepared according to any one of the foregoing methods, can be converted into a light colored to white pigment by heating the Monox in the presence of the halogen gas at elevated temperatures below the temperature at which the Monox would tend to sinter or fuse. It also has been found that the halogen-containing gas can contain up to about 65% by volume of an oxidizing gas, based on the total volume of the halogen and oxidizing gases, to reduce materially the silicon halides, especially silicon tetrahalides, produced during halogenation with retention of the original fibrous structure exhibited by the brown Monox. Subsequent to treatment with halogen or halogen-oxidizing gas, the resulting product can be treated with steam or water to remove essentially all of the halogen adsorbed on or bound to the surfaces of the particles of the treated Monox without adversely affecting the now light to white color of or the physical struc-
ture exhibited by the new pigment. The products produced by the methods of the present invention are essentially, particulate, solid, amorphous silicas, and fibrous and non-fibrous and opacified or may not contain more for amounts of halogen, hydroxyl and/or nitrogen groups.

During the reaction, the halogen apparently reacts with the silicon metal of the solid, disproportionated silicon monoxide to remove it as a silicon halide, such as silicon tetrahalide, which can be subsequently condensed or recovered and used as a starting material for making various silicon-containing products. Another by-product can be hexahalodisiloxane. The removal of the silicon by halogen does not affect the fibrous structure of the original Monox particles which apparently retain their original shape, length and particle size although some small voids may appear in the fibers. Some of the bound nitrogen originally present in the starting Monox may still be present in the halogenated Monox. In some cases an increase is observed in the surface area of the particulate material as compared to the surface area of the original brown Monox.

When an oxidizing gas is used as a diluent for the halogen gas in an amount below a maximum of 66% by volume of the total volume of the halogen and oxidizing gases, it has been found that removal of the silicon metal still occurs but to a somewhat lesser degree. At the same time, a portion of the silicon is oxidized to silica. The product produced, depending on the amount of oxidizing gas used, is still light colored to white. However, the light colored products can be made almost pure white by a subsequent treatment with only halogen gas. The use of an oxidizing gas with the halogen gas is desirable sometimes in order to reduce the amount of silicon halides obtained which may tend to present storage and disposal problems. It, therefore, is a way in which the ratio of the new white pigment to silicon halides produced can be adjusted depending on product needs and uses.

Subsequent treatment of the halogenated or halogenated-oxidized Monox with steam serves to remove all or essentially all of the halogen contained in the new pigment without detracting from the color or physical structure of said pigment. Elastomers containing the steam-treated, halogenated or halogenated-oxidized Monox are just as satisfactorily reinforced as when the original, untreated Monox is used except that they are light or white in color, or that their original color has not been materially affected, rather than being brown in color as would be the situation if untreated brown Monox was used. It is generally necessary to remove from the pigment all or essentially all of the halogen introduced in the halogenation step to obtain optimum physical properties in the elastomers such as the hydrophobicity of rubbers and plasticized vinyls with which the pigment may be compounded. However, the halogenated or halogenated-oxidized Monox materials will also find many uses as intermediates in making reinforcing pigments for elastomeric compositions as set forth more particularly in copending applications of Roger W. Strassburg filed of even date, Serial Nos. 554,648 and 554,640, entitled “Methods and Compositions of Matter” and “Compositions and Methods,” respectively.

The halogen gas or halogen-oxidizing gas treated solid Monox product contains a residual amount, usually up to about 3%, by weight of halogen which can be removed entirely or almost entirely by treatment with steam at elevated temperatures. By removing entirely or almost entirely all of the halogen means that insufficient halogen remains in the steamed product to produce a noticeable effect in materials with which the product is compounded or is present in such an amount it may be merely considered an adventitious impurity. It is not precisely known how the halogen is bound to the particles of the new pigment. It is believed that it may be attached or chemically bound to the surface of the particles by splitting Si-Si bonds in areas of lattice imperfections and/or by the reaction of SiCl4 with residual OH groups sometimes found on silica materials. It may be that the halogen is both adsorbed and bound. Treatment with steam serves to hydrolyze the halogen contained in the new pigment and to liberate it as hydrogen halide. For example, the minor amount of halogen contained in the Monox after treatment can be represented by the following formula:

\[ (e-(n+m+p))SiO2 + m \left[ SiO_{2-n}^{+1} \right] + \]

\[ n \left[ SiO_{2-n}^{+2} \right] + p \left[ SiO_{2-n}^{+3} \right] + \]

where e = total number of SiO2 groups before reaction of Monox with halogen, m = number of SiO2 groups with 1 valence link to halogen groups, n = number of SiO2 groups with 2 valence links to halogen groups, p = number of SiO2 groups with 3 valence links to halogen groups, \( v = \) the number of valence links of halogen attached to silica,

\[ m + 2n + 3p \]

is divisible by \( v \) and

\[ m + 2n + 3p = \text{number of halogen groups} \]

The silica containing the minor amount of halogen in the lattice can also be represented by the following formula:

- Si-O-Si-Halogen
- Si-O-Si

or (SiO Hal)_x where x is an integer. Two or three halogen atoms may be attached to a silicon atom. Halogen atoms may be on adjacent silicon atoms. When treated with steam and the like, the halogen radical will be replaced with an OH radical to give the following structure:

- Si-O-Si-OH
- Si-O-Si

or

- Si-O-Si-OH
- Si-O-Si

Nearby OH groups may also condense if the conditions and temperatures are proper. The pigments at the end of the halogenation step, the halogenation-oxidation step, and/or the steaming step are light colored to white. A feature of the method of the present invention is that the halogenation process serves to remove any traces of metallic or other ions which were contained in the silicon monoxide gas as impurities from the carbon and other source of silicon monoxide gas which may condense with the SiO gas also to affect adversely the purity and color of the Monox and the new pigment.

The halogen gas used can be chlorine, fluorine, bromine, or iodine gas or mixtures thereof. It is much preferred to use chlorine because it is more economical to use than the other halogenes, it is not as reactive as fluorine and it does have as high a molecular weight as iodine. The halogen is employed in an amount sufficient to react with the silica contained in the original brown Monox. Thus, in general, at least 2 moles of halogen are required for 1 gram-atom of silicon although an excess is preferably employed to insure complete reaction and to remove any traces of impurities.
The oxidizing gas used with the halogen gas to control the amount of silicon-halides produced can be oxygen, water vapor, air or any other oxidizing gas which will oxidize at least part of the silicon in the Monox without adversely affecting its properties such as structure and surface area and will serve to control the amount of silicon-halides produced. It is much preferred to use oxygen since the silicon halide vapor is not thereby diluted to such an extent that it is difficult to condense. For example, when using a material such as air containing a large amount of nitrogen, the silicon halide vapor is as diluted with nitrogen that it is difficult to condense and recover. It is noteworthy that the use of an oxidizing gas up to the amounts indicated below will serve to increase the yield (weight) of pigment obtained without changing the fibrous structure exhibited by the original Monox while decreasing the yield of silicon halides, especially silicon tetrahalide. The pigment will also contain some halogen but in a lesser amount than when halogen gas alone was used. When using the oxidizing gas with the halogen-containing gas, they are preferably mixed together in a volume ratio below about 2:1, or, in other words, the volume of oxidizing gas, exclusive of inert gas such as nitrogen, when for example air is used, should be less than 66% of the total volume of the halogen and oxidizing gases. Preferably the volume of oxidizing gas should not exceed 50% of the total. At or above 66% of oxidizing gas, a reduction in the total amount of fibers and a shortening of the length of the fibers of the resulting pigment occurs due to melting and/or sintering such that a large proportion becomes non-fibrous and amorphous in shape. It is not desired to obtain non-fibrous or spherical particles since they reduce the reinforcing ability of the resulting pigment in elastomeric products such as rubber. Moreover, as the amount of the oxidizing gas with respect to the halogen gas is increased above a ratio of 2:1, the color of the pigment becomes tan probably due to a surface oxidation of the silicon metal without a complete oxidation to the core of the silicon metal particle. This tan color, however, can be removed by subsequent treatment with halogen gas at the temperatures indicated herein so long as the color has not become “locked in” by fusing a layer of silica over a silicon particle surface. A feature of the method of the present invention is that the original brown Monox need not be freshly prepared before treatment with halogen gas. It can be permitted to stand in air at room temperature where some of the silicon is oxidized to form a film of silica over the surface of the silicon particles. So long as the film has not been produced at or subjected to high temperatures to cause fusion, subsequent halogenation will remove the remaining silicon metal. However, if the oxide film has been fused, halogen gas or the halogen-oxidizing gas mixture cannot penetrate the fused silica layer to remove the silicon and provide a light-colored white product.

The use of steam is much preferred to the use of water, hot or cold, to remove halogen since the reaction with steam is conducted in the vapor phase and the resulting pigment is more readily handled and more easily dispersed in elastomers than one treated with water. Treatment of the halogenated product with steam to remove halogen may proceed at elevated temperature for a period of time and in an amount sufficient to remove all or essentially all of the halogen contained in the products, although, in general, temperatures for steam treatment may be lower than those required for halogenation since the halogen is readily removed. It has been found that a relatively short treatment time, usually not more than from about 2 to 3 hours, where the original halogenation requires, will remove the residual halogen. Moreover, if the original “Monox” contained bound nitrogen, some of the nitrogen is probably removed by the steam with the halogen but additional steam will be required to remove all or essentially all of this bound nitrogen so that only traces, if any, of bound nitrogen remain in the product after analysis and do not materially affect the properties of the resulting steamed product when compounded in elastomers or other matrices to be employed.

This bound nitrogen will be released in the form of ammonia. It is not absolutely necessary to remove all of the nitrogen. If desired, only a substantial amount need be removed. A product containing the same can be used for many purposes and in some instances the presence of nitrogen is of particular advantage since the nitrogen confers some alkalinity on the product so that it is not as acid as a product containing no nitrogen, for example, a product derived from Monox made in a pure inert gas or in a somewhat impure inert condensing gas containing hydrogen.

In the process of halogenating the Monox, it can be placed in a tube in an amount sufficient to fill the tube without interfering with the passage of the halogen containing gas and then treated with said gas at a temperature of at least about 600° C. Since the reaction with halogen is exothermic, the temperature of the reaction should not be allowed to reach the fusion temperature of the Monox and preferably should not go above about 1100° C. to avoid fusing or sintering of the particles of the Monox. While the melting point of silica varies from about 1470 to 1710° C. and of silicon is about 1420° C., the fusion or softening point of the Monox particles or new pigment will be somewhat less due to their high surface area and small particle size. However, their precise fusion or sintering point is not determinable readily with precision and, accordingly, it is preferred that the reaction temperature should not exceed about 1100° C. at which temperature appreciable fusion or sintering does not occur. Although the silicon halide gas produced during the reaction serves to dilute the halogen and to cool it and the Monox or the product somewhat during the reaction, it still may be necessary to externally cool the tube or other reaction chamber to maintain the temperature below about 1100° C. Alternatively, cooling may be effected by reducing the volume or amount of halogen gas to reduce the rate of reaction, or by diluting the halogen gas with a cool inert gas such as nitrogen. On the other hand, the minimum temperature required to obtain improvement in color should be about 600° C. Below 600° C. no perceptible change in the brown color of the Monox is observed. Preferably, the operating temperature should be from about 700° to 900° C. in which range a white colored pigment is produced under the best operating and economic conditions. The silicon tetrahalide produced can be collected in an ice-cooled reactor or by other means during the run and used in further processing of making silicon-containing compounds which are well known in the art.

In place of using a single tube in a batch-type process, the Monox may be continuously treated in an inclined rotary kiln wherein the Monox is introduced at the upper end of the kiln and proceeds gradually downward while the halogen gas is introduced at the opposite end of the kiln and passes up through the kiln to react with the Monox. Alternatively, the Monox and halogen gas can pass concurrently through the kiln. Processes using fluidized beds can also be employed. Such processes are continuous and thereby contribute to the economy of the operation. Still other apparatus and techniques can be employed. It will be appreciated that the kiln should be suitably protected to prevent contamination or corrosion from the halogen used and should contain suitable means to prevent leakage of such gas which might be hazardous.

When an oxidizing gas is used with the halogen gas, it will be employed in the amounts indicated above and within the same temperature range, although the treatment time may be from 1½ to 3 times as long as when
using halogen alone. Subsequent to the treatment with the halogen gas, the pigment can be treated in the same or other equipment with steam at a temperature above 100° C. above the condensation point of the steam and up to below the fusion point of the pigment or chlorinated Monox, preferably up to about 1100° C., to remove all or essentially all of the halogen.

The amount of the treating gases used and the time of treatment will vary according to the size of the apparatus employed, the amount of pigment involved, degree of agitation and the reaction temperatures produced, being careful to avoid a condition where the reaction or treating temperatures are as high as the fusion point of the Monox or the silicon dioxide containing compound being treated.

As pointed out hereinabove, the halogen-containing compounds of the present invention can be used as starting materials or intermediates in other processes to provide surface-coated pigments useful as reinforcing agents in elastomeric compounds or can be treated with a material such as steam to remove the halogen contained therein and used directly in elastomeric materials. Additionally, the halogen-free light colored to white pigment can be coated with various materials such as alcohols, amines, silicone resins and the like, and the like coating of the pigment before it is incorporated into the elastomer. While this invention has been described with particular reference to treatment of the brown fibrous or substantially fibrous forms of Monox which offer the greatest improvement in elastomeric products, particularly rubber, it is apparent that the above remarks will apply to the brown non fibrous or substantially spherical forms of Monox which reinforce to a lesser degree but which are still useful as a reinforcing pigment and can also be used as a loading material, filler, and so forth in various elastomers. Moreover, the light colored to white halogen-free pigments prepared by the method of the present invention will also find utility in other organic compositions such as in thermoplastics and thermosetting plastics, in hard rubbers, in rigid vinyls, in resins, in ceramic compositions, in insulating compositions, in lubricants, etc.

The pigments of the present invention are particularly useful in reinforcing elastomeric materials. Examples of elastomeric materials which can be used with these pigments are natural and synthetic vulcanizable rubbers such as natural rubber, which is essentially a polymer of isoprene, butadiene, and polyisoprene and the rubbery polymers of open-chain conjugated dienes, dienes especially having from 4 to 8 carbon atoms such as butadiene-1,3, isoprene, 2-3 dimethyl butadiene-1,3, and the like, or the rubbery copolymers, terpolymers and the like of these and similar conjugated dienes with each other or with at least one copolymerizable monomeric material such as isobutylene, styrene, acrylonitrile, methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, 2-vinyl pyridine, etc. The polymeric diene elastomers generally contain at least 50% by weight of the diene and preferably contain from about 55 to 85% by weight of the diene. However, copolymers, terpolymers and other multicomponent polymers containing as little as 35% or less by weight of diene can also be employed, for example, terpolymers containing about 35% butadiene-1,3, 35% styrene, and 30% acrylonitrile and copolymers containing about 47.5% isobutylene and 21.2% isoprene. Still other polymeric materials can be used such as the polymers and copolymers of styrene, vinyl chloride, vinyl chloride-vinylidene chloride, vinylidene chloride, vinyl chloride-vinyl acetate, isobutylene, and so forth. Moreover, there can be used polymers having curable acid groups and formation of the polymerization of an open-chain aliphatic conjugated diene and an olefinically unsaturated carboxylic acid, by the reaction of a polymer of a diene with a carbonyl supplying reagent preferably in the presence of a catalyst, by copolymerization of a diene with an olefinically unsaturated copolymerizable compound hydrolyzable to form an acid group, by copolymerization of an olefinically unsaturated diene with an olefinically unsaturated carboxylic acid, by hydrolysis of an allyl ester of acrylic acid or by copolymerization of a major amount of a monoxide or isolefin with a copolymerizable compound hydrolyzable to form groups containing bound —COOH. Still other polymers can be employed such as those formed by the copolymerization of dienes with allyl acrylates, by the polymerization of allyl acrylates alone and by the polymerization of an allyl acrylate with at least one other olefinically unsaturated monomer which then are hydrolyzed to obtain curable —COOH groups. In place of polymers having —COOH groups, polymers having groups such as COOR, COCN, CONH₂, COONH₄, and COO⁻Me, where Me is a metal, and the like which are convertible to COOH groups by amonolysis, hydrolysis, or similar reaction, for example, by treating such polymers with dilute mineral acids, HCI or H₂SO₄, or concentrated or preferably dilute KOH or NaOH, can also be employed after such groups have been converted to a curable COOH group. Polymers having SO₂H, SO₃H or OH- or change the way to other acid groups, or derivatives thereof convertible to the free acid on hydrolysis and which likewise can be cross-linked, cured or vulcanized can also be used. Polymeric vulcanizable synthetic rubbers formed by the polymerization of an acrylic acid ester, for example ethyl acrylate or butyl acrylate, or mixtures of acrylic acid esters or by the copolymerization of an acrylic acid ester with a chlorine-containing monomer such as a minor amount of chloroethyl vinyl ether, vinyl chloride, or dichloro dihydro ethylene or with acrylonitrile, ethylene or styrene can likewise be used. Polyester urethanes can also be usefully employed; they are formed by the reaction of an organic diisocyanate compound with a hydroxy containing polystyrene reaction product of a dibasic acid and a glycol and cross linked, cured or vulcanized by means of a poly-functional hydroxyl or polyhydroxy compound. The silicone rubbers can also be employed. Mixtures of the foregoing elastomers can also be employed. Elastomeric materials other than those specifically mentioned above are also useful.

In reinforcing elastomeric materials, a minor amount of the treated halogen-free pigment of the present invention is used with a major amount of the elastomeric material. Preferably, in order to obtain the best results an elastomeric composition will contain from about 25 to 45% by weight of the pigment of this invention to from about 75 to 5% by weight of the elastomer, exclusive of other compounding ingredients.

Appropriate compounding ingredients such as other fillers, processing aids, accelerators, vulcanizing agents, curing agents, cross-linking agents, stabilizers, retarders, plasticizers, antioxidants, resins, dyes, color pigments, fungicides, and so forth may be employed with the elastomeric compositions.

For the purposes of the present invention it is to be understood that the word "curing" in the specification and claims is intended to cover vulcanization, cross-linking, condensing, fusing or other treatment of the elastomer by which it, whether a conjugated diene, polyester urethane, or carbonyl containing polymer, acrylate, vinyl or other elastomer or organic polymer, is converted, under the action of heat, light, or vulcanizing, cross-linking, condensing and/or other agent, into a useful material as it is well known to those skilled in the art. "Curing" is also intended to cover the method of vulcanizing polystyrene soften on heating and harden or toughen on cooling as well as the method employing elastomers which vulcanize, cross-link, etc., at room temperature and below.

The products of the present invention will find utility
as a filler or reinforcing pigment in compositions for tire treads, white sidewalls of tires, V-belts, gloves, shoe soles, heels, printing rollers, cutless bearings and wherever it is desired to reinforce an elastomer with a light colored to white solid silicon monoxide derivative. It is noteworthy that the use of the pigment treated as described herein to remove halogen and particularly in the form of fibers with or without bound nitrogen, not only affords good reinforcing properties to rubbery materials comparable to those imparted by carbon black compounds but also permits the obtinment of light colored to white elastomeric materials. Moreover, since the pigment obtained according to the present invention has little covering power, elastomeric compositions reinforced with such pigment can be pigmented or dyed to provide colored elastomeric materials which are not obtainable with carbon black nor to any degree with the original brown Monox. Since the pigment of the present invention has the same index of refraction as benzene, for it disappears in benzene when added thereto, or as the elastomeric material in which incorporated, it does not tend to adversely color the elastomer as would the original brown Monox or an opaque pigment such as carbon black or to color the elastomer without reinforcing it as does titanium dioxide. Rather, the pigments produced by the methods disclosed herein are somewhat translucent and accordingly can be combined with various organic and inorganic color pigments such as phthalocyanine blue, phthalocyanine green, chrome red, chrome yellow, titanium dioxide, ultramarine blue, and the like in minor amounts to give colored reinforced elastomeric products of great utility. It is only necessary to use a very minor amount of the coloring pigment so that the reinforcing properties of the present pigment are not lost.

The following examples will serve to illustrate the invention with more particularity to those skilled in the art:

**EXAMPLE I**

Brown, substantially fibrous Monox was prepared by the reaction of anthraquinone coal and sand in an arc furnace to produce SiO gas which was condensed without appreciable turbulence using commercial (oil pump) nitrogen gas containing about 1% by volume of ammonia. The Monox contained about 4.07% nitrogen and 0.07% Cl, as an impurity from the residual condensing gases, laboratory atmosphere, etc. A 30 gram sample of this brown, substantially fibrous Monox was placed in a "Vycor," high (90-92%) silica glass, tube having means to heat and cool the same. The inlet end of the tube was connected to a suitable source of chlorine gas while the exit end was connected to an ice-cooled receiver for condensation of silicon tetrachloride. The tube was heated and 33 g. of chlorine gas was introduced into it and passed through the Monox at a temperature of 300° C. and at 500° C. In each instance no change in color of the Monox occurred. The runs were repeated at 600, 700 and 800° C. It then was noted that at 600° C. a light gray product was produced, the reaction zone slowly moving down the tube as indicated by the progressively growing section of white pigment in the reaction zone. The light gray product may still be useful where a white product is not absolutely required. At 700° C. and at 800° C. the samples were white and colored bands appeared on the exit end of the reaction tube which were water soluble and were found to contain ferric, sodium and ammonium chlorides on analysis. The iron, sodium and ammonium apparently had been contained in the original brown Monox as impurities and had sublimed as chlorides during the reaction. Similar runs were conducted in which the temperature was allowed to run up to 1100°. The resulting products were still white. All of the products from about 600° to 1100° were light colored to white in color and showed no change in the length of size of the fibrous particles of the original Monox although their surface area had been increased in some instances as shown by nitrogen absorption probably due to removal of some of the non fibrous particles or silicon in the fibrous particles. At well above 1100° C. sintering and melting of the particles occurred with reduction in the length of the fibers and a reduction in size although the product obtained was white. X-ray diffraction patterns of the samples treated within the effective operating temperature range showed that the silicon ring exhibited in the pattern given by the starting Monox was missing. The light colored to white products as prepared herein contained about 3% of chlorine and the balance essentially SiO2. During the runs at temperatures of from about 600 to 1100° C., crude silicon tetrachloride condensed in the ice cooled receiver on the exit end of the reaction tube. When distilled, the crude product was shown to contain about 80% silicon tetrachloride, about 2.2% hexachlorodisiloxane and the balance a residue of mixed silicon halides.

**EXAMPLE II**

This example was similar to Example I, above, except that the SiO gas was condensed in a mixture of commercial nitrogen gas and hydrogen gas, the reaction temperature was maintained at 800° C. and oxygen gas in various amounts was mixed with the chlorine gas prior to treating the starting brown Monox which contained 0.22% nitrogen, probably as an impurity from the furnace reactants or gases. The mixture of chlorine and oxygen gases was passed through the Monox having a surface area of 100 m²/g. over a period of about 100-160 minutes. The amounts of the reactants used, the products obtained and the properties of the products obtained are shown in Table A below:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Volume Ratio</th>
<th>Monox, g.</th>
<th>Product, g.</th>
<th>Product Surface Area, m²/g.</th>
<th>Cl₂ Added</th>
<th>Crude SiCl₄, g.</th>
<th>Obtained</th>
<th>Product, % Cl Content</th>
<th>Color of Product</th>
<th>Physical Structure of Product, compared to Starting Monox</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0 4 21 20 114</td>
<td>60 49.5 2.11</td>
<td>White</td>
<td>No Change</td>
<td>Do</td>
<td>Increase in non-fibrous particles, rounded ends of fibers.</td>
<td>Many non-fibrous particles, sintering, fibers forming globules.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1 2 29 20 118</td>
<td>55 27.0 0.82</td>
<td>Slightly off white.</td>
<td>Do</td>
<td>Do</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1 1 31 29 119</td>
<td>20 17.1 0.71</td>
<td>White</td>
<td>Slightly off white.</td>
<td>Do</td>
<td>Increase in non-fibrous particles, rounded ends of fibers.</td>
<td>Many non-fibrous particles, sintering, fibers forming globules.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>2 1 30 35 84</td>
<td>30 2.9 0.33</td>
<td>White</td>
<td>No Change</td>
<td>Do</td>
<td>Increase in non-fibrous particles, rounded ends of fibers.</td>
<td>Many non-fibrous particles, sintering, fibers forming globules.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>2 0 31 27 86</td>
<td>31 2.7 0.41</td>
<td>White</td>
<td>No Change</td>
<td>Do</td>
<td>Increase in non-fibrous particles, rounded ends of fibers.</td>
<td>Many non-fibrous particles, sintering, fibers forming globules.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

C. over a period of 50-80 minutes. No change in color of the Monox occurred and no condensate appeared in the ice-cooled receiver. Additional runs with similar amounts of chlorine were made with the temperatures at 400° C. and at 500° C. Electron micrographs showed no change in structure until the ratios of oxygen to chlorine became 2:1. With the higher ratios of oxygen, the ends of the individual fibers became non fibrous and/or spherical because of melting.
2,865,778

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As the oxygen content of the gas mixture increased to the volume ratio of 2 oxygen to 1 chlorine, the color of the final product became tan because the oxygen formed a silica coating over the silicon particles. Further reaction with chlorine gas removed this tan color except when oxygen alone was used in which case the color was “locked in.” This example illustrates the fact that oxygen can be mixed with the chlorine gas up to below a ratio of about 2:1, with production of a light colored white product having essentially the same physical form as the original or starting Monox and with a reduction in the amount of crude silicon tetrachloride produced. These products also contained about 1–2 percent of chlorine. Moreover as the ratio of oxygen to chlorine becomes 2:1 or greater, or oxygen alone is used, sintering of the particles of Monox occurs in the times indicated. The sintering is probably due to the fact that, in the presence of oxygen or high concentrations of oxygen, the surfaces of the silicon particles are in a very active state or at a higher temperature than the temperature of the mass which facilitates sintering, fusion or agglomeration of the particles because it is noted that, when chlorine is used alone or oxygen is used with chlorine in a volume ratio of up to below 2:1, no visible evidence of sintering occurs at 800° C. or even up to 1100° C. Accordingly, it is apparent that oxygen should not be mixed in large amounts with the chlorine if sintering is to be avoided.

EXAMPLE III

The pigment obtained from Monox chlorinated at 700–800° C. according to Example I, above, was treated for about one hour with steam at a temperature above 100° C. in the tube described in Example I and which was at a temperature of about 800° C. Hydrogen chloride was given off. After completion of the run the product was analyzed. The analysis showed that it still contained some nitrogen, as was present in the starting material, and also contained 0.07% by weight of chlorine showing that all of the chlorine introduced by chlorination had been removed. Subsequent treatment for an hour with steam under the same conditions resulted in the removal of some of the nitrogen as ammonia. This product was also analyzed and shown to contain 0.05% by weight of chlorine and 2.38% by weight of nitrogen. Both products had the same fibrous structure and particle size of the starting brown Monox and white chlorinated Monox of Example I and were white in color.

EXAMPLE IV

Two samples of brown substantially fibrous Monox were halogenated at 700–800° C. and then treated with steam according to the methods of Examples I and III, above, to obtain a white product. One (A) was analyzed and shown to contain 2.38% by weight of nitrogen and 0.05% chlorine and the other (B) was analyzed and found to contain 0.26% by weight of chlorine and 3.61% nitrogen. 60 parts by weight of each pigment were then compounded with 100 parts of natural rubber, 0.5 part dianil dine, 0.2 part stearic acid, and 0.2 part sulfur on a rubber mill at 330° F. for 15 minutes. The batches were then cooled to 160° F. and mill mixed with 5 parts zinc oxide, 1½ parts stearic acid, 1 part pine oil, 1 part phenyl beta naphthylamine, 1½ parts diocetyl amine, 1 part benz thiadiazyl sulfide and 3 parts sulfur. After compounding, separate batches of the compositions were cured at 280° F. for varying periods of time to form light colored vulcanizates and then tested. The results on test are shown in Table B below:

<table>
<thead>
<tr>
<th>Cure, Min.</th>
<th>Tensile Strength, p. s. l.</th>
<th>Elongation at break, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>450</td>
<td>225</td>
</tr>
<tr>
<td>20</td>
<td>1,080</td>
<td>275</td>
</tr>
<tr>
<td>60</td>
<td>1,200</td>
<td>278</td>
</tr>
<tr>
<td>90</td>
<td>1,050</td>
<td>250</td>
</tr>
</tbody>
</table>

Table C

<table>
<thead>
<tr>
<th>PIGMENT</th>
<th>Izod</th>
<th>T1 °C</th>
<th>T2 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A–1</td>
<td>1.33</td>
<td>96.0</td>
<td>170.5</td>
</tr>
<tr>
<td>C–1</td>
<td>1.13</td>
<td>96.6</td>
<td>190.0</td>
</tr>
</tbody>
</table>

T1 is the transition temperature of the formulation, the point at which a piston under a given load supported by granules of the formulation in a cup moves when the cup is heated. T2 is the fusion temperature of the formulation, the point at which the granules have apparently become fused and are extruded through a hole in the bottom of the cup. It, thus, is seen that vinyl compositions containing the products produced by the method of the present invention have transition and fusion temperatures equal to or higher than those exhibited by a composition containing precipitated silica. The impact resistances of vinyl compositions containing the products of the method of the present invention were almost twice as great as that exhibited by a vinyl formulation containing only precipitated silica. This example, thus, shows that the pigments produced by the method of the present invention can be employed in vinyl compositions to produce useful light colored products or products which can be colored with color pigments.

EXAMPLE VI

Substantially fibrous brown solid silicon monoxide, Monox, prepared by condensing SiO gas without appreciable turbulence in an atmosphere of commercial nitrogen gas containing a minor amount of hydrogen gas was chlorinated at 700–800° C. and then treated with steam according to the methods of Examples I and III. It was analyzed and found to contain no measurable amount of chlorine, i.e., Cl=0.08%. If any nitrogen was present, it was present only as a trace. The resulting white fibers...
product was then formulated and tested in a silicone rubber composition as follows:

Component:  
Parts by weight  

<table>
<thead>
<tr>
<th>Component</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Above steam stripped chlorinated Monox</td>
<td>40</td>
</tr>
<tr>
<td>Methyl silicone rubber (Linde Air Products Co.,</td>
<td>100</td>
</tr>
<tr>
<td>silicone gum stock X-95)</td>
<td></td>
</tr>
<tr>
<td>Dicumyl peroxide</td>
<td>2</td>
</tr>
</tbody>
</table>

Stress strain at R. T.; cure 15° @ 300° F., press; 24 hrs. @ 300° F. oven:

| Tensile, p. s. I.                                         | 590             |
| Modulus, 200%                                             | 580             |
| Elongation, percent                                       | 200             |
| Stress strain at 212° F.                                   | 400             |
| Modulus, 200%                                             | 400             |
| Elongation, percent                                       | 175             |

This example illustrates that the pigment produced by the method of the present invention can be usefully employed in silicone rubber compositions to make light colored produral electrical insulating materials.

In summary, the present invention teaches that light colored to white silicone and oxygen containing fibrous or nonfibrous materials may be obtained by the treatment of brown Monox with halogen gas in a certain elevated temperature range to remove the Si in the Monox as a silicon halide. The resulting product exhibits the same structure as the starting material and may therefore be of a higher surface area. It is useful as an intermediate in preparing pigments for reinforcing elastomers. The small amount of halogen obtained in such product can readily be removed by subsequent treatment with steam to produce products directly useful as a reinforcing pigment. Moreover, the treatment with halogen can be controlled by employing oxygen to reduce the amount of silicon halide obtained while still giving a light colored to white product having an increased silica content and the same physical form. The product prepared by the method of the present invention will have great utility as a pigment which not only reinforces elastomeric materials but also permits the obtaining of light to white and even variously colored elastomeric materials.

What is claimed is:

1. The method which comprises treating a brown, particulate, disproportionated solid selected from the group consisting of silicon monoxide and silicon monoxide containing from about 1 to 8% by weight of bound nitrogen at a temperature of from about 600° C. to below the halogenation point of said solid with a halogen gas in an amount sufficient to react with at least a portion of the silicone in said solid to form gaseous silicone halides and to leave a light colored to white, solid, particulate, silicon dioxide composition containing chlorine in an amount not in excess of about 3% by weight.

2. The method according to claim 1 in which said halogen is chlorine.

3. The method according to claim 1 containing the additional step of treating said silicon dioxide composition with fluid H₂O in an amount and at a temperature sufficient to remove essentially all of the halogen from said silicon dioxide composition without fusing the same.

4. The method according to claim 3 in which said fluid H₂O is steam.

5. The method according to claim 1 in which said halogen gas contains additionally an oxidizing gas in an amount up to below 66% by volume of the total volume of said halogen and oxidizing gases.

6. The method according to claim 5 containing the additional step of treating said silicon dioxide composition with fluid H₂O at a temperature below the fusion point of said silicon dioxide composition without fusing the same.

7. The method according to claim 6 in which said fluid H₂O is steam.

8. The method which comprises treating a brown, particulate, substantially fibrous, disproportionated solid selected from the group consisting of silicon monoxide and silicon monoxide having from about 1 to 8% by weight of bound nitrogen at a temperature of from about 700° to about 900° C. with chlorine gas in an amount sufficient to react with at least a portion of the silicon in said solid to form substantially gaseous silicon tetrachloride and to leave a light colored to white, solid, particulate, substantially fibrous silicon dioxide composition containing chlorine in an amount not in excess of about 3% by weight.

9. The method according to claim 8 containing the additional step of treating said silicon dioxide composition with steam at a temperature below the fusion point of said silicon dioxide composition and in an amount sufficient to remove essentially all of the chlorine contained in said silicon dioxide composition.

10. The method according to claim 9 in which said steamed silicon dioxide composition containing bound nitrogen from said nitrogen containing silicon monoxide is treated with additional steam in an amount sufficient and at a temperature below the fusion point of said silicon dioxide composition in an amount sufficient to remove essentially all of the chlorine contained in said silicon dioxide composition.

11. The method according to claim 8 in which said chlorine gas contains additionally up to about 50% by volume of oxygen gas based on the total volume of said chlorine and oxygen gases.

12. The method according to claim 11 containing the additional step of treating said silicon dioxide composition with steam at a temperature below the fusion point of said silicon dioxide composition and in an amount sufficient to remove essentially all of the chlorine contained in said silicon dioxide composition.

13. The method according to claim 12 in which said steamed silicon dioxide composition containing bound nitrogen from said nitrogen containing silicon monoxide is treated with steam in an additional amount and at a temperature sufficient to remove essentially all of the chlorine from said silicon dioxide composition.

14. A composition characterized by being light colored to white in color, particulate, and consisting of silicon dioxide substantially free of metallic impurities and containing halogen attached to the silicon of said silicon dioxide in an amount not in excess of about 3% by weight.

15. A composition characterized by being particulate, substantially free of metallic impurities, light colored to white and solid and being selected from the group consisting of silica and silica containing bound nitrogen groups, the number of atoms of nitrogen in said nitrogen groups being substantially equivalent to the number of nitrogen atoms in particulate, solid silicon monoxide containing from about 1 to 8% by weight of bound nitrogen and said particulate, light colored to white solid containing halogen attached to the silicon of said particulate, light colored to white solid and being present in an amount not in excess of about 3% by weight.

16. A composition according to claim 15 in which said halogen is chlorine.

17. A composition according to claim 15 characterized further by being substantially fibrous.

18. A composition according to claim 17 in which said halogen is chlorine.

19. A composition according to claim 17 in which said particulate, light colored to white solid has been treated with fluid H₂O in an amount sufficient to remove essentially all of said halogen from and without fusing said particulate, light colored to white solid.

20. A composition according to claim 18 in which the fibers of said substantially fibrous composition have a ratio of length to width of at least about 10:1 to 50:1,
have an average length of at least about 50 to 600 milli-
microns and have a surface area of at least about 60 to
200 square meters per gram.

21. A composition according to claim 18 in which said
particulate, light colored to white solid has been treated
with fluid H₂O in an amount and at a temperature suffi-
cient to remove essentially all of said chlorine from and
without fusing said particulate, light colored to white
solid.

22. A composition according to claim 21 in which the
fibers of said substantially fibrous composition have a
ratio of length to width of at least about 10:1 to 50:1;
have an average length of at least about 50 to 600 milli-
microns and have a surface area of at least about 60 to
200 square meters per gram.

23. The method which comprises treating a solid com-
prising silicon monoxide at a temperature of from about
600° C, to below the fusion point of said solid with a
halogen gas in an amount sufficient to react with at least
a portion of the silicon in said solid to form gaseous
silicon halides and to leave solid silicon dioxide contain-
ing halogen in an amount not in excess of about 3% by
weight.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,865,778

Roger W. Strassburg

December 23, 1958

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 27, for "vacuum" read -- vacuum --; column 4, line 68, after "does" insert -- not --.

Signed and sealed this 2nd day of June 1959.

(SEAL)
Attest:
KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents