PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ^{5} **:**
C01F 5/22, C08K 9/04
C09C 1/02, C08K 3/22

A1

(11) International Publication Number: **WO 92/12097**

(43) International Publication Date: 23 July 1992 (23.07.92)

(21) International Application Number: PCT/US91/09629

(22) International Filing Date: 20 December 1991 (20.12.91)

(30) Priority data:

633,817	26 December 1990 (26.12.90)	US
633,818	26 December 1990 (26.12.90)	US

(71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).

(72) Inventor: MERTZ, Steven, F. ; 2472 North Rath Road, Ludington, MI 49431 (US).

(74) Agent: SELBY, Robert, W.; The Dow Chemical Company, P.O. Box 1967, Midland, MI 48641-1967 (US).

(81) Designated States: AT (European patent), BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), SE (European patent).

Published
With international search report.

(54) Title: MAGNESIUM HYDROXIDE HAVING STACKED LAYER, CRYSTALLINE STRUCTURE AND PROCESS THEREFOR

(57) Abstract

Magnesium hydroxide having a particulate, crystalline structure with a thickness of 30 to 200 Angstroms, and a median particle size of up to about 1 micron prepared by a process in which less than or greater than an equivalent amount of alkaline material is reacted with a magnesium salt in a concentrated aqueous mixture thereof. The magnesium hydroxide is especially useful in providing flame retardancy in admixture with thermoplastic resins.

30,000X———1µm

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria
AU	Australia
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CS	Czechoslovakia
DE	Germany
DK	Denmark
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GN	Guinea
GR	Greece
HU	Hungary
IT	Italy
JP	Japan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
LI	Liechtenstein
LK	Sri Lanka
LU	Luxembourg
MC	Monaco
MG	Madagascar
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
NL	Netherlands
NO	Norway
PL	Poland
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SN	Senegal
SU	Soviet Union
TD	Chad
TG	Togo
US	United States of America

MAGNESIUM HYDROXIDE HAVING STACKED LAYER, CRYSTALLINE STRUCTURE AND PROCESS THEREFOR

Magnesium hydroxide can be produced by adding a water-soluble alkaline material to an aqueous solution of a magnesium salt at atmospheric pressure or slightly above and temperatures from slightly above room temperature to about 100 degrees centigrade (°C) or slightly higher. The precipitate which forms on standing forms small crystals whose largest dimension does not exceed about 5 microns and whose thickness is in the range of about 300 to about 900 angstrom units. The use of inorganic fillers such as magnesium hydroxide to provide flame retardancy in thermoplastic resins is known.

The prior art does not disclose magnesium hydroxide particles structurally characterized by a predominant multilayered, stacked, crystalline structure. The magnesium hydroxide of the invention can be prepared by a batch or continuous mixing process, as disclosed herein, wherein each layer of the multilayered structure is a single crystal of magnesium hydroxide that forms on the (0001) plane of brucite. The stacked layers form elongated particles where the plane of each layer is perpendicular to the long axis of the cylindrical particle.

The particulate magnesium hydroxide of the invention is particularly suited for use in conjunction with thermoplastic synthetic resins to provide flame retardancy thereto. In this application, the solid particles of magnesium hydroxide can be utilized subsequent to coating with a surfactant or can be utilized without any coating thereon.

Figures 1 and 2 are reproductions of photographs taken magnified 30,000 times of a sample of magnesium hydroxide produced respectively in a batch process and in a continuous process. The multilayered, stacked, crystalline structure is evident.

Figure 3 is a graph showing the particle size distribution of two samples of a magnesium hydroxide produced by the continuous process of the invention, as shown in lines labeled "A" and "B". The particle size distribution of a prior art magnesium hydroxide is shown in the line identified as "C".

Figures 4 and 5 are reproductions of photographs taken magnified 10,000 and 30,000 times, respectively, of a sample of magnesium hydroxide produced in the continuous process of the invention.

The present invention includes a batch or continuous method for the production of a magnesium hydroxide having a particulate, crystalline structure with a fine plate-like form, characterized by:

(a) mixing a concentrated aqueous mixture of an alkaline material and a magnesium containing salt, wherein the mixture comprises 20 to 60 percent by weight of a mixture of reactants comprising an alkaline material and a magnesium containing salt and said alkaline material is used in a stoichiometric excess of the amount present of said magnesium containing salt and

(b) heating the mixture at ambient pressure to convert said magnesium containing salt to magnesium hydroxide with a plate-like form 30 to 200 Angstroms thick and a median particle size of up to 1 micron.

The method of preparing the novel particulate, crystalline structure magnesium hydroxide characterized predominantly as multilayered and stacked, comprises mixing an aqueous solution of a magnesium salt, described in examples 6 through 9, with an alkaline material and heating the mixture at ambient pressure and elevated temperature to precipitate the magnesium hydroxide. The temperature used for heating the mixture is between 40°C and 120°C, preferably, 50°C to 100°C, and most preferably, 65°C to 80°C. At temperatures of less than 40°C, the reaction time is unsatisfactorily slow.

In the process of the invention, less than an equivalent amount of an alkaline material is mixed in an aqueous medium with a magnesium containing salt and the mixture reacted by heating at ambient pressure to precipitate magnesium hydroxide. Alternatively, in the process of the invention, less than an equivalent amount of a magnesium containing salt is mixed in an aqueous medium with an alkaline material and the mixture heated at ambient pressure to convert the magnesium containing salt to magnesium hydroxide. Generally, the alkaline material and the magnesium salt reactants are combined in the proportion of 0.7 to 1.30 equivalent of one of said reactants per equivalent of the other of said reactants, preferably, a proportion of 0.85 to 1.15 equivalent, and most preferably, 0.95 to 1.05 equivalent. In the processes of the invention, the reactants (alkaline material and magnesium containing salt) are present in a high concentration. Generally, the reactants are present at a total solids content of 20 to 60 percent by weight based upon the total weight of reactants and aqueous medium preferably, the total solids of reactants is 20 to 45 percent by weight, and most preferably, 25 to 35 percent by weight.

Generally, the precipitation reaction at elevated temperature is continued for 1 to 4 hours, preferably, 1 to 3 hours, and, most preferably, 1 to 2 hours. Thereafter, the precipitated magnesium hydroxide is separated by filtration or other convenient means from the aqueous medium and from the soluble salts dissolved therein. Washing the precipitate with water and subsequent re-filtration may be necessary to appropriately reduce the concentration of residual salts associated with the precipitated magnesium hydroxide. Generally, the residual soluble salt concentration is reduced to 0.05 percent by weight to 5 percent by weight, preferably 0.2 percent to 3 percent by weight and, most preferably, 0.1 percent to 1 percent by weight.

Should it be desirable to reduce the specific surface area of the particulate magnesium hydroxide of the invention, the magnesium hydroxide, subsequent to reaction, filtration, and washing, may be redispersed in water and further reacted in a post reaction by heating at elevated temperature. The reaction mixture concentration, temperature, and time for reaction are the same as previously indicated for the initial precipitation reaction. A substantial reduction in specific surface area is obtained by this post reaction, provided the magnesium hydroxide is post-reacted in an aqueous medium which is substantially free of dissolved salts. Generally, a soluble salt concentration of 0.05 percent to 5 percent by weight, preferably, 0.2 percent to 3 percent by weight, and, most preferably, 0.1 percent to 1 percent by weight is required in the reactant mixture during the post reaction. The preferred particulate magnesium hydroxide of the invention is characterized by a predominant distinctive multi-layered, stacked, crystalline structure, a median particle size produced in the batch process of about 1 micron, and a particle size distribution in which 70 percent of the magnesium hydroxide particles are within 0.6 to 3.9 microns or a continuous process in which about 80 percent of said particles are within 0.3 to 1.6 microns.

Any magnesium salt which is soluble in water can be used for making the $Mg(OH)_2$ of this invention by the procedure defined above. Representative inorganic magnesium salts are MgF_2, $MgCl_2$, $MgBr_2$, MgI_2, $MgBrO_3$, $MgBrO_4$, $MgClO_3$, $MgClO_4$, $MgCrO_4$, $MgFeO_4$, $MgSo_4$, $MgSo_3$, MgS_2O_3, $Mg(MnO_4)_2$, $MgMoO_4$, $Mg(NO_3)_2$. Magnesium salts of organic acids can also be used, provided they are water soluble. Representative salts of organic acids include those of fatty acids having from 1 to about 6 carbon atoms, such as magnesium formate, acetate, propionate, butyrate, pentanoate, hexanoate, citrate or a salt of an aromatic acid such as magnesium benzoate, salicylate and phthalate.

The preferred magnesium salts are those of sulfuric, nitric and hydrochloric acid, the most preferred salt being $MgCl_2$, because of its ready availability from sources all over the world.

Preferably, the magnesium salt is a brine comprising an aqueous solution of an alkali metal or an alkaline earth metal halide salt including magnesium chloride. More specifically, both natural and synthetic brines which contain at least about 15 total weight percent of the chlorides of magnesium and calcium are preferred. The brine usually contains at least 2 percent by weight of magnesium chloride.

The alkaline material can be an amine or a slaked calcined dolomite or an alkali or alkaline earth metal hydroxide or mixtures thereof.

The use of calcined dolomite in the production of magnesium hydroxide has certain inherent advantages over the use of calcined limestone. Among such advantages are the high yield of magnesium hydroxide when dolomite is employed since, when calcined, it contains about 1 mole of MgO per mole of CaO and, therefore, when reacted with a magnesium chloride-containing brine and the magnesium oxide becomes hydrated, it yields substantially two times the amount of magnesium hydroxide which would be produced from the reaction of calcined limestone with an equal quantity of the brine. Dolomite is relatively plentiful, being found in a substantially high degree of purity, and is often located conveniently near natural brine sources, as for example, in the state of Michigan, U.S.A.

Disadvantages, however, have heretofore been associated with the production of magnesium hydroxide as a precipitate employing dolomite as a raw material, salient among which have been its poor filterability when separating it as a filter cake from the mother liquor and when dewatering it following washing or following reslurrying of the washed cake. The low solids, i.e., the low density of the filter cake produced during filtration (often as low as 30 to 35 percent solids) is also undesirable and particularly undesirably is the high contamination of the product produced from water-slaked dolime unless promptly used, particularly calcium contamination, which has also been associated with contamination of the magnesium hydroxide precipitate from ingredients present in the brine, especially chlorides and borates. Dewatering refers to the step of concentrating an aqueous slurry of magnesium hydroxide, this step being commonly carried out by employing a rotary vacuum filter.

Among the larger uses of magnesium hydroxide is the manufacture of periclase-type refractory products which cannot tolerate an appreciable contamination of the magnesium hydroxide. Difficulties arising from contamination by calcium have been particularly troublesome. As much as 1.5 percent calcium oxide in the ignited magnesium hydroxide product is generally considered a maximum contamination for commercial acceptance and not more than 1 percent CaO is preferred. A number of large deposits of dolomite are substantially pure, e.g., the Cedarville quarries of Michigan, which by analysis shows this deposit to consist of about 1.03 moles of $CaCO_3$ per mole of $MgCO_3$ with a small percent of inerts. The only concern regarding contamination in the use of such dolomite as a source material is calcium contamination of the magnesium hydroxide.

In addition to a conventional batch process of precipitation, the magnesium hydroxide of the invention can be prepared utilizing ultrasonic mixing means preliminary to heating the mixture to complete the conversion reaction or precipitation of magnesium hydroxide. Precipitation of magnesium hydroxide utilizing ultrasonic vibration produced with a wave direction coinciding with the direction of precipitation of the salts is known. These waves increase rapidity of precipitation owing to the fact that the waves are propagated in the same direction as that in which the precipitates fall. It is well known that the device for producing the ultrasonic or supersonic waves can be disposed on, for example, a pipeline for discharging water from a decanting reactor.

If desired, the magnesium hydroxide of the invention may be treated with an anionic surfactant to form solid particles of magnesium hydroxide coated with the surfactant. This form of the magnesium hydroxide of the invention is more preferred when using it as a flame retardant or flame-retarding filler for thermoplastic resins or in water-soluble paints. The coating process can be performed by contacting the magnesium hydroxide with an anionic surfactant or by contacting either or both the reactants with an anionic surfactant prior to the production of the magnesium hydroxide of the invention. For example, an aqueous solution of a desired amount of an anionic surfactant is mixed with solid particles of the magnesium hydroxide under conditions such that they contact each other intimately, for example, by agitating them sufficiently, or by thermal treatment of an aqueous slurry at 120 to 250°C. A solid powder of magnesium hydroxide coated with the anionic surfactant is formed upon removal of water. The surfactant is chemically adsorbed onto the surface of the solid particles of the magnesium hydroxide. This can lead to improved properties (as compared to uncoated magnesium hydroxide) when the magnesium hydroxide is incorporated in thermoplastic synthetic resins or in water-soluble paints.

The amount of the anionic surfactant to be applied as a coating can be adjusted for optimum results. Solid magnesium hydroxide powder of this invention coated by using an aqueous surfactant solution containing 5 millimoles to 30 millimoles per liter of water, of the surfactant is preferred. For example, the amount of the anionic surfactant adsorbed onto the solid particles of the magnesium hydroxide of this invention is preferably 1/4 to 3 times, more preferably 1 to 2.5 times the amount (X in millimoles) required to coat the entire surface of the solid particles (one gram) with a monolayer of the surfactant molecules. The amount X (millimoles) can be calculated in accordance with the following equation.

$$X = \frac{Y}{6.02 \times C} \quad \text{(millimoles)}$$

wherein C is the absolute value of the adsorption cross-sectional area $[(A)^2]$ per molecule of the anionic surfactant used and Y is the absolute value of the specific surface area (m^2/g) of the magnesium hydroxide of this invention.

According to this invention, there can be provided a composition containing uncoated magnesium hydroxide of this invention or the magnesium hydroxide of this invention coated with an anionic surface active agent. For example, compositions having improved properties, especially those useful for melt shaping, can be provided by incorporating the coated or uncoated magnesium hydroxide of this invention in a thermoplastic synthetic resin, preferably those having great hydrophobicity and great non-polarity, as a flame retardant or flame-retarding filler in an amount of 50 to 250 parts by weight (pbw) per 100 pbw of the resin. Examples of the thermoplastic synthetic resin include styrene resins such as a homo- or co-polymers of styrene, olefin resins such as homo- or co-polymers of olefins, polyester resins, polycarbonate resins, nylon resins, acetal resins, and blends of these resins. These compositions may be provided in the form of melt-shaped articles. Furthermore, by incorporating the coated or uncoated magnesium hydroxide of this invention in paints or lacquers in an amount of 5 to 150 pbw per 100 pbw of the resin vehicle, paint compositions having improved properties can be obtained.

Various conventional additives may further be incorporated in the thermoplastic synthetic resin composition or in paint compositions in accordance with this invention.

Examples of these additives are coloring agents (organic and inorganic pigments) such as isoindolinone, cobalt aluminate, carbon black, or cadmium sulfide, other fillers such as calcium carbonate, alumina, zinc oxide or talc; antioxidants such as 2,6-di-t-butyl-4-methylphenol, 2,2'-methylenebis (4-methyl-6-t-butylphenol), dilauryl thiodipropionate or tridecyl phosphite; ultraviolet absorbers such as 2-hydroxy-4-methoxy benzophenone, 2(2'-hydroxy-5'-methylphenyl) benzotriazole, 2-ethylhexyl-2-cyano-3,3-diphenyl acrylate, phenyl salicylate or nickel-bisoctyl phenyl sulfide; plasticizers such as di-2-ethyl hexyl phthalate, di-n-butyl phthalate, butyl stearate, or epoxidized soybean oil; and lubricants such as zinc stearate, calcium, aluminum and other metal soaps, or polyethylene wax.

These additives can be used in customary amounts. For example, the amount of the coloring agent is 0.1 to 3 pbw; the amount of the other filler is up to 20 pbw; the amount of the antioxidant or ultraviolet absorber is 0.001 to 5 pbw; the amount of the plasticizer is up to 20 pbw; and the amount of the lubricant is up to 10 pbw. All these amounts are based on 100 pbw of the resin component.

The anionic surface active agent (surfactant) used to coat the magnesium hydroxide of this invention includes, for example, alkali metal salts of higher fatty acids of the formula

$$RCOOM$$

wherein R is an alkyl group containing 8 to 30 carbons atoms, and M is an alkali metal atom, alkyl sulfate salts of the formula

$$ROSO_3M$$

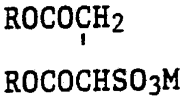
wherein R and M are the same as defined above, alkylsulfonate salts of the formula

$$RSO_3M$$

wherein R and M are the same as defined above, alkylaryl sulfonate salts of the formula

$$R\text{-aryl-}SO_3M$$

wherein R and M are the same as defined above, and sulfosuccinate ester salts of the formula



$$\begin{array}{l} ROCOCH_2 \\ \quad\;\, | \\ ROCOCHSO_3M \end{array}$$

wherein R and M are the same as defined above. These anionic surfactants can be used either alone or in admixture of two or more.

Specific examples of the surface active agent are sodium stearate, potassium behenate, sodium montanate, potassium stearate, sodium oleate, potassium oleate, sodium palmitate, potassium palmitate, sodium laurate, potassium laurate, sodium dilaurylbenzenesulfonate, potassium octadecylsulfate, sodium laurylsulfonate or disodium 2-sulfoethyl α-sulfostearate.

Alternatively, the magnesium hydroxide of the invention can be coated with a fatty acid ester of a polyhydric alcohol. For some purposes, such coating is superior to the use of a coating of an anionic surface active agent such as an alkali metal salt of a higher fatty acid. The polyhydric alcohol can have 2 to 6 hydroxyl groups and is represented by such compounds as ethylene glycol, propylene glycol, glyceryl, trimethylolpropane, pentaerythritol and dipentaerythritol. Of these polyhydric alcohols, those of the neopentyl series such as dipentaerythritol, pentaerythritol, and trimethylolpropane, are preferably in view of their stability at high temperatures. A saturated fatty acid having 4 to 24 carbon atoms, preferably, a saturated straight chain fatty acid having 8 to 18 carbon atoms or a mixture of acids having the above defined carbon atoms on the average can advantageously be used as the fatty acid constituent. The fatty acid ester of the polyhydric alcohol can be a completely esterified compound wherein all hydroxyl groups in the starting polyhydric alcohol are esterified or a partial ester, wherein only a part of the hydroxyl groups are esterified.

The use of magnesium hydroxide in thermoplastic polymer materials has replaced the prior use of a mixture of antimony trioxide and a halide compound such as a vinyl chloride resin as additives useful for incorporating flame retardancy in thermoplastic materials. This is because the use of magnesium hydroxide in thermoplastics as a flame retardant results in thermoplastic composites which emit less smoke and less toxic smoke as compared to thermoplastic composites containing halogenated flame retardant additives. The prior art use of a combination of antimony trioxide and a halide as flame retardant additives in a thermoplastic material also results in the evolution of a halogen gas during the molding operation utilized to form specific objects from the thermoplastic resins so compounded for flame retardancy. The evolution of halogen gas leads to the corrosion of molding machines and metal molds and results in a toxic environment for workers involved in the molding operation. The incorporation of magnesium hydroxide in thermoplastic materials to provide flame retardancy is superior in accomplishing the desired result without the deleterious effect of the evolution of a halogen gas during the molding operation.

Suitable thermoplastic resins for use with the magnesium hydroxide of this invention include: polypropylene, propylene-ethylene copolymer, polyethylene, ethylenepropylene copolymer, ethylenevinyl acetate copolymer, polystyrene, acrylonitrile-butadiene-styrene copolymer, acrylonitrile-styrene copolymer. Especially suitable are polyolefins such as polypropylene, propylene-ethylene block or random copolymers, high-density or low-density polyethylene.

The following examples illustrate the various aspects of the invention but are not intended to limit its scope. Where not otherwise specified throughout this specification and claims, temperatures are given in degrees centigrade and parts, percentages, and proportions are by weight.

Example 1

An aqueous lime slurry containing 23 percent by weight calcium hydroxide and 17 percent by weight magnesium hydroxide and having a total solids content of 40.5 percent by weight was pretreated with an anionic surfactant sold under the trade name Silwet 7604 at a ratio of 1.5 grams surfactant per liter of lime slurry by mixing the lime slurry with the surfactant for 30 minutes. Silwet is sold by the Union Carbide Corporation.

An aqueous brine solution containing 8.9 percent by weight magnesium chloride, 17 percent by weight calcium chloride, 0.9 percent by weight sodium chloride, and lesser amounts of other salts including those of strontium, lithium, boron, and iron having a total solids content of 27.8 percent by weight was similarly treated with Silwet 7604 (an organo modified polydimethyl siloxane) anionic surfactant at a ratio of 0.42 grams of surfactant per liter of brine solution utilizing the process described above.

The anionic surfactant treated lime slurry was heated in a vessel under agitation to 71°C and, thereafter the brine solution at ambient temperature was pumped into said vessel containing the lime slurry over a period of 95 minutes. The pH of the mixture was 6.6 at the end of the brine addition. The temperature of the vessel containing the mixture was maintained at about 71°C. After all the brine had been added, the addition of heat to the vessel was terminated and the contents of the vessel were thereafter stirred for a period of about 18 hours. A small additional volume of brine was then added to adjust the pH of the slurry to 7.0. The amount of lime slurry utilized to combine with the brine was 0.9 equivalent. The slurry was subsequently filtered and washed to remove calcium chloride.

Upon analysis, the magnesium hydroxide particles recovered from this batch process were found to have a median particle size of 0.87 micron, as determined with a Micromeritics Sedigraph which combines the principle of sedimentation with X-ray detection in order to obtain this measurement of particle size. The particles consist of stacked layers, each of which is a single crystal of magnesium hydroxide having a unit layer thickness of 30 to 200 Angstroms. Electron diffraction patterns recorded from individual particles show that the crystal structure of this layered material is brucite, a known form of magnesium hydroxide. There are small crystallographic rotations between adjoining layers. The individual particles are not single crystals; rather they are highly-ordered stacks of thin crystals. Each layer of brucite forms on the (0001) plane, and the stacked layers form elongated particles whose long dimension, normal to the (0001) plane, is the brucite c-axis. The long dimension of the particle is typically 0.25 to 1 micron, and the width of the particle is typically about half the length. When viewed perpendicular to the c-axis, many of the particles are seen to taper toward the ends. The shape of each magnesium hydroxide layer is irregular and varies from triangular to hexagonal to circular. Hence, the layer diameter within a single particle varies form 100 to 1700 Angstroms, and, therefore, the particle diameter varies. This variation in particle diameter gives the particles a distinct layered corrugated appearance when viewed perpendicular to the c-axis.

Example 2

Example 1 was repeated except that the lime slurry and the brine solution were not treated with an anionic surfactant prior to combination and heating to precipitate the magnesium hydroxide. The resulting magnesium hydroxide particles upon determination of particle size in accordance with the method utilized in Example 1, had a median particle size of 1.0 micron and substantially similar morphology.

Example 3

Example 2 was repeated except that the lime solution was added to the brine solution. This was heated to 71°C under agitation and, thereafter, the lime solution at ambient temperature was added to the vessel containing the brine slurry. The resulting magnesium hydroxide had a median particle size of 1.1 microns and substantially similar morphology.

Example 4

Example 1 was repeated except that a continuous process was used and the lime slurry of Example 1 was pretreated with Silwet 7604 anionic surfactant at a ratio of 2.6 grams surfactant per gallon of slurry in accordance with the procedure described in Example 1. The brine solution described in Example 1 was similarly pretreated with this anionic surfactant at a ratio of 2.6 grams surfactant per gallon of brine solution.

Thereafter, both the lime slurry and the brine solution at ambient temperature were pumped simultaneously into the ultrasonic mixing chamber of a "Model A" Sonolator homogenizer manufactured by Sonic Engineering Corporation, Norwalk, Connecticut. The ratio of the speed of the pump utilized to pump the brine solution into the ultrasonic mixing chamber over that of the pump utilized to pump the lime slurry into the ultrasonic mixing chamber was 3.5 which is equivalent to providing a 14 percent excess of brine solution over the stoichiometric ratio required to react the brine solution with the lime slurry. In this example, the brine solution and the lime slurry were pumped into the ultrasonic equipment mixing chamber at ambient temperature and at a pressure of 400 to 500 pounds per square inch. The mixed lime slurry and brine solution were thereafter post-treated by placing the mixture in a tank fitted with an agitator and a steam coil. Agitation and heating at the boiling point were continued for a period of two hours and, thereafter, the mixture was filtered and washed with water.

The magnesium hydroxide product obtained was found to have a median particle size of 0.61 micron with 90 percent by volume of the particles having a particle size of less than 0.93 micron and 10 percent of the particles having a particle size of less than 0.42 microns.

Example 5

Example 4 was repeated except that no anionic surfactant was used to pretreat the lime slurry and the brine slurry. Substantially similar results are obtained.

Example 6

An aqueous lime slurry containing 23 percent by weight calcium hydroxide and 17 percent by weight magnesium hydroxide and having a total solids content of 40.5 percent by weight was pretreated with Silwet 7604 anionic surfactant at a ratio of 1.3 grams surfactant per gallon of lime slurry by mixing the lime slurry with the surfactant for 30 minutes.

An aqueous brine solution containing 8.9 percent by weight magnesium chloride, 17 percent by weight calcium chloride, 0.9 percent by weight sodium chloride, and lesser amounts of other salts including those of strontium, lithium, boron, and iron having a total solids content of 27.8 percent by weight was similarly treated with Silwet 7604 anionic surfactant at a ratio of 1.3 grams of surfactant per gallon of brine solution utilizing the process described above.

The anionic surfactant treated lime slurry was pumped into the ultrasonic mixing apparatus described above. Similarly, the anionic surfactant brine solution was pumped from a vessel containing the brine solution to the ultrasonic mixing apparatus. The "Model A" Sonolator used as an ultrasonic mixing means was set at a pressure of 400 psi. The ratio of the speed of the pump used to pump the brine solution into the ultrasonic mixing chamber over that speed of the pump used to pump the lime slurry into the ultrasonic mixing chamber was 3.5, which is equivalent to providing a 14 percent excess of brine solution to the lime slurry. The amount of lime slurry utilized to combine with the brine was 0.9 equivalent. Subsequent to ultrasonic mixing, the reaction mixture was transferred to a post treatment mixing tank and heated for 2 hours at 105°C. The precipitated magnesium hydroxide was recovered from the aqueous medium by filtration and washing of the precipitate to remove salts.

Upon analysis, the magnesium hydroxide particles recovered from this continuous process were found to have a median particle size of 0.7 micron, as determined with a Micromeritics Sedigraph which combines the principle of sedimentation with X-ray detection in order to obtain this measurement of particle size. About 80 percent of the particles were within 0.3 to 1.4 microns. The particles consist predominantly of individual plate-like formed particles many of which are 0.25 to 0.3 micron in width. Each of the particles is a single crystal of magnesium hydroxide having a unit layer thickness of 30 to 200 Angstroms. Electron diffraction patterns recorded from individual particles show that the crystal structure of these particles are brucite, a known form of magnesium hydroxide.

Example 7

Example 6 was repeated except that the lime slurry and the brine solution were not treated with an anionic surfactant prior to mixing by ultrasonic means and heating to precipitate the magnesium hydroxide. The resulting magnesium hydroxide particles upon determination of particle size in accordance with the method utilized in Example 6, had a median particle size of 0.8 micron and substantially similar morphology.

Example 8

Example 6 was repeated except that the lime slurry and the brine solution were heated to 71°C prior to mixing by ultrasonic means. Substantially similar median particle size and morphology are obtained in comparison with that obtained in Example 6.

Example 9

Example 8 was repeated except that the lime slurry and the brine solution were not treated with an anionic surfactant prior to mixing and heating to precipitate the magnesium hydroxide. Substantially similar median particle size and morphology are obtained as compared to Example 8.

1. A batch or continuous method for the production of a magnesium hydroxide having a particulate, crystalline structure with a fine plate-like form, characterized by:

(a) mixing a concentrated aqueous mixture of an alkaline material and a magnesium containing salt, wherein the mixture comprises 20 to 60 percent by weight of a mixture of reactants comprising an alkaline material and a magnesium containing salt and said alkaline material is used in a stoichiometric excess of the amount present of said magnesium containing salt and

(b) heating the mixture at ambient pressure to convert said magnesium containing salt to magnesium hydroxide with a plate-like form 30 to 200 Angstroms thick and a median particle size of up to 1 micron.

2. The method of Claim 1, wherein the mixture is heated at a temperature of 40°C to 120°C and the alkaline material is a water soluble alkaline material selected from the group consisting of an amine, an alkaline earth metal hydroxide, and an alkali metal hydroxide.

3. The method of Claim 2, wherein the mixture is heated at a temperature of 50°C to 100°C and said magnesium containing salt is an inorganic magnesium salt selected from the group consisting of magnesium fluoride, magnesium chloride, magnesium bromide, magnesium iodide, magnesium bromate, magnesium bromite, magnesium chlorate, magnesium chlorite, magnesium chromate, magnesium sulfate, magnesium sulfite, $MgFeO_4$, MgS_2O_3, $Mg(MnO_4)_2$, $MgMoO_4$, and magnesium nitrate.

4. The method of Claim 2, wherein the mixture is heated to a temperature of 65°C to 80°C and the magnesium salt is a salt of an organic acid selected from the group consisting of salts of fatty acids having from 1 to about 6 carbon atoms, selected from the group consisting of magnesium formate, acetate, propionate, butyrate, pentanoate, hexanoate, citrate or a salt of an aromatic acid, selected from the group consisting of magnesium benzoate, salicylate, and phthalate.

5. The method of Claim 2, wherein the mixture comprises 20 to 45 percent by weight of said mixture of reactants.

6. A magnesium hydroxide produced by the batch method of Claim 1, having a particle size distribution in which about 70 percent of said particles are within 0.6 to 3.9 microns.

7. A magnesium hydroxide produced by the continuous method of Claim 1 having a median particle size of about 0.7 micron, and a particle size distribution in which about 80 percent of said particles are within 0.3 to 1.6 microns.

8. Solid particles of the magnesium hydroxide particles of Claim 7 coated with an anionic surface active agent, the magnesium hydroxide having a particulate, crystalline structure with a particle size distribution in which about 70 percent of the particles are within 0.6 to 3.9 microns.

9. A thermoplastic synthetic resin composition containing the magnesium hydroxide of Claim 7 coated or uncoated with an anionic surface active agent, the magnesium hydroxide having a particulate, crystalline structure with a particles size distribution in which 70 percent of the particles are within 0.6 to 3.9 microns.

10. The method of Claim 1, wherein the mixture is heated at a temperature of 40°C to about 100°C to convert said magnesium containing salt to magnesium hydroxide.

11. The method of Claims 1 through 10 wherein the alkaline material is calcium oxide.

12. The method of Claims 1 through 10 wherein the alkaline material is calcined dolomite.

13. The method of Claims 1 through 12 wherein the magnesium hydroxide has predominantly a multilayered and stacked crystalline structure.

30,000X——1μm

FIG. 1

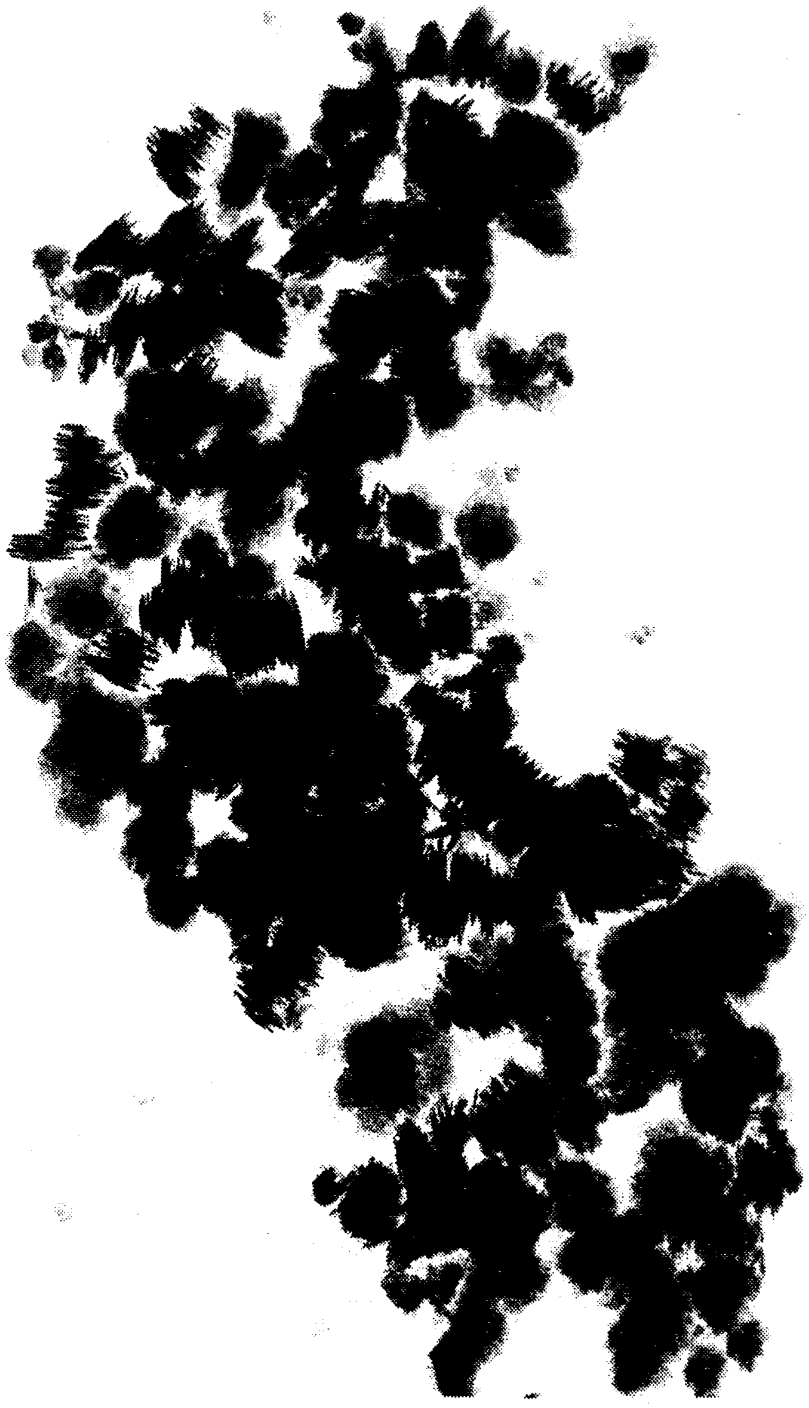


FIG. 2

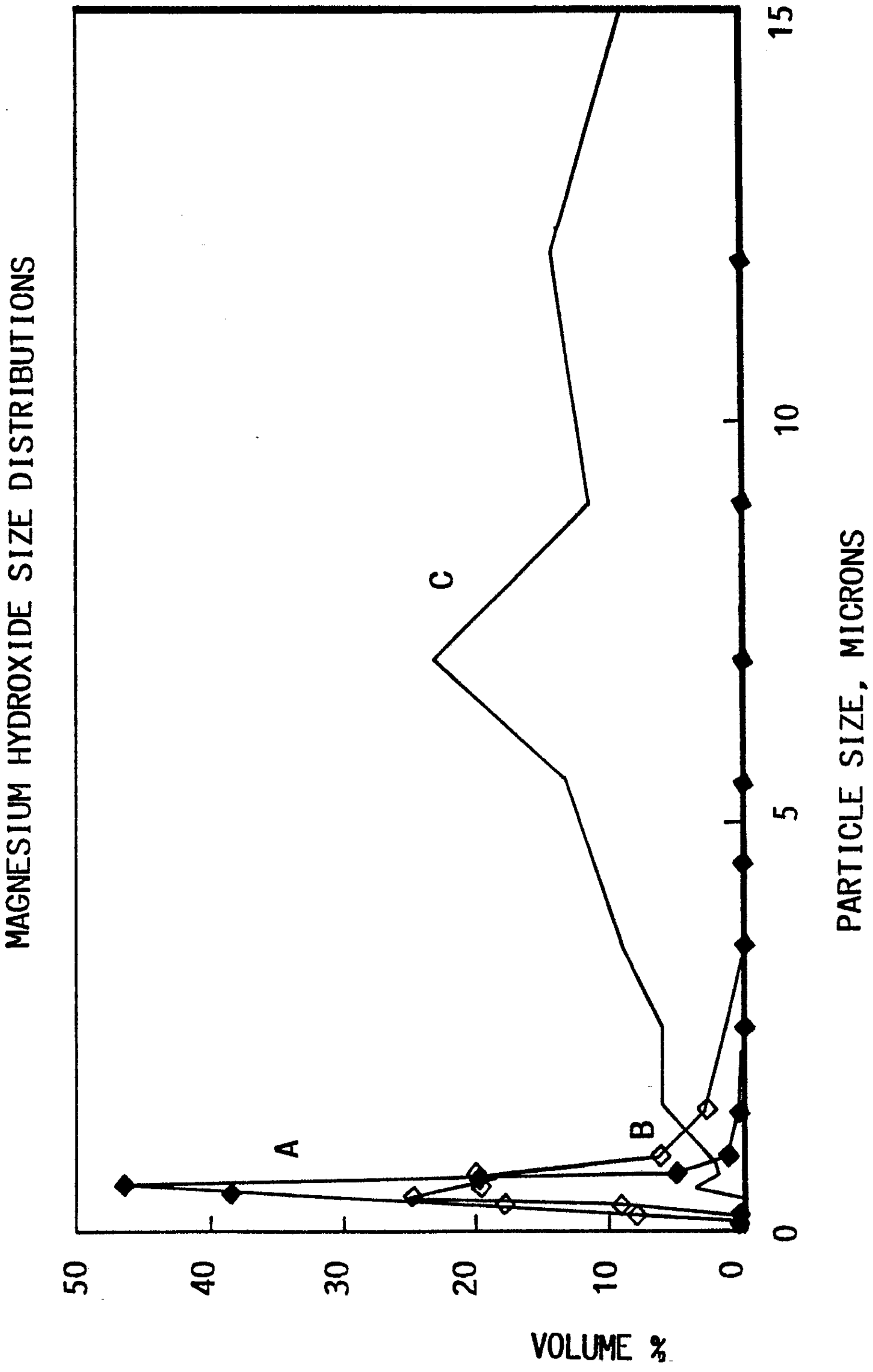
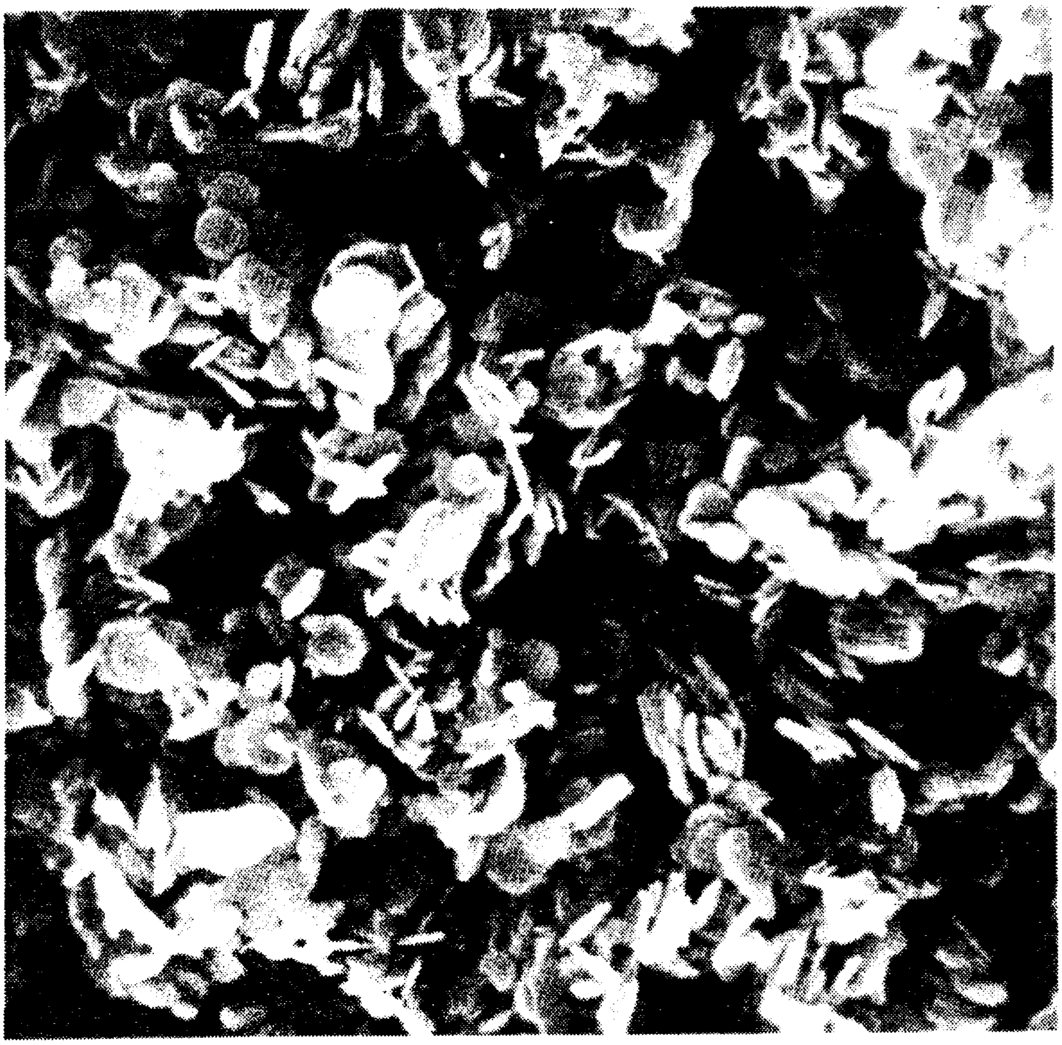
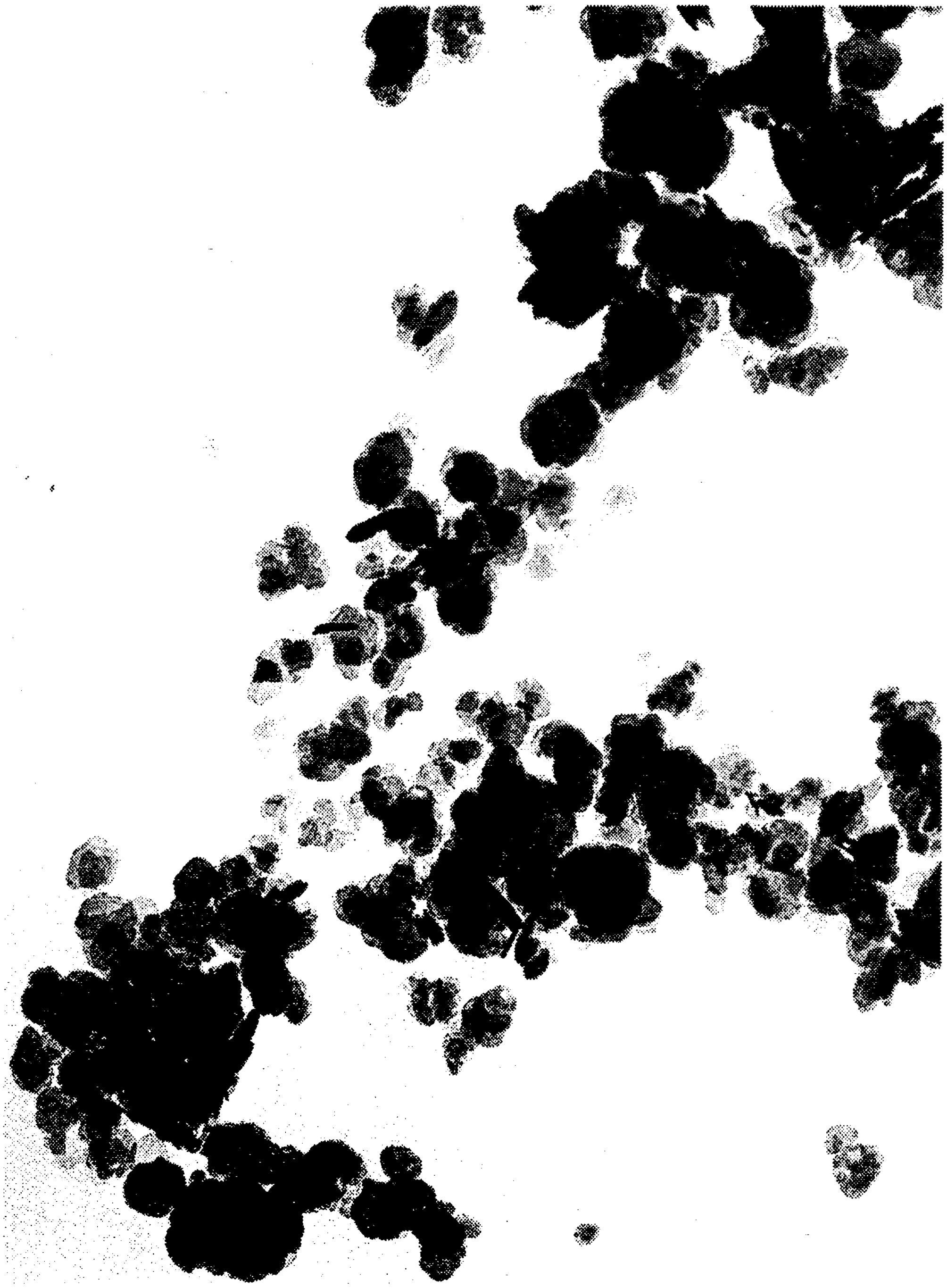

MAGNESIUM HYDROXIDE SIZE DISTRIBUTIONS
A
B
C
VOLUME %
50
40
30
20
10
0
PARTICLE SIZE, MICRONS
0
5
10
15

FIG. 3



10,000 X µm

FIG. 4



30,000X ___ 1μm

FIG. 5

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/09629

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C01F5/22; C08K9/04; C09C1/02; C08K3/22

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C01F ; C08K ; C09C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	EP,A,0 365 347 (KYOWA CHEMICAL INDUSTRIES) 25 April 1990 see the whole document	1-7,9, 10,13
Y	see the whole document ---	8,11,12
A	EP,A,0 384 603 (KYOWA CHEMICAL INDUSTRY) 29 August 1990 see page 4, line 5 - line 27; claim 1; example 1 ---	1-7,10, 13
Y	DE,B,2 659 933 (KYOWA CHEM IND) 30 October 1980 see column 6, line 11 - column 8, line 31 ---	8
Y	DE,A,2 646 965 (TAKAHASHI) 21 April 1977 see the whole document ---	8
Y	EP,A,0 038 891 (DALMIA INST OF SCIENT AND IND RES) 4 November 1981 see the whole document ---	11,12

-/--

° Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 16 APRIL 1992	Date of Mailing of this International Search Report 07.05.92
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer ZALM W.E.

2

Form PCT/ISA/210 (second sheet) (January 1985)

International Application No PCT/US 91/09629

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 214 494 (ASAHI GLASS COMP) 18 March 1987 see the whole document ---	6,7
A	US,A,3 111 376 (PATTON ET AL.) 19 November 1963 ---	
A	US,A,3 301 633 (STOWE ET AL.) 31 January 1967 ---	
A	US,A,3 366 451 (WALDRON ET AL.) 30 January 1968 ---	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9109629 SA 55537

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 16/04/92

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0365347	25-04-90	JP-A-	2111625	24-04-90
EP-A-0384603	29-08-90	JP-A-	2212314	23-08-90
		CA-A-	2009715	10-08-90
		US-A-	5039509	13-08-91
DE-B-2659933	30-10-80	JP-A-	52115799	28-09-77
		JP-B-	63048809	30-09-88
		JP-A-	51140946	04-12-76
		JP-B-	52016735	11-05-77
		CA-A-	1090537	02-12-80
		DE-A,B,C	2624065	16-12-76
		FR-A,B	2314892	14-01-77
		GB-A-	1514081	14-06-78
		US-A-	4098762	04-07-78
		US-A-	4145404	20-03-79
DE-A-2646965	21-04-77	JP-A-	52109542	13-09-77
		JP-A-	52049254	20-04-77
		GB-A-	1510237	10-05-78
		NL-A-	7611511	20-04-77
		US-A-	4126593	21-11-78
EP-A-0038891	04-11-81	AU-B-	548576	19-12-85
		AU-A-	6521280	03-09-81
		CA-A-	1157231	22-11-83
		US-A-	4370422	25-01-83
EP-A-0214494	18-03-87	JP-A-	62123014	04-06-87
		US-A-	4695445	22-09-87
US-A-3111376		None		
US-A-3301633		None		
US-A-3366451		None		

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82