UNITED STATES PATENT OFFICE

This invention relates to a metal powder, e. g., magnesium powder having form and particle size such that it is fitted for use as a component of flares, incendiary and tracer bullets and shot, pyrotechnic signals, flashlight bombs, and the like devices, and as a reagent in organic synthesis.

In accordance with this invention it is contemplated to produce a powder that, while exhibiting a utility-value for the purposes above mentioned, not substantially less, and in some cases even greater, than previously known and standard powders, is free from the notorious explosion hazards of such standard powders, to the degree that it may fairly be considered a new product. And it is incidentally a product which is adapted for incorporation in some of the devices referred to, without the need for the preliminary treatment required where such standard powders are used.

Incidentally, the invention includes the idea of packaging a given quantity of the powder of desired characteristics as to particle size and distribution, in a container that may be readily and safely handled during certain otherwise dangerous stages of manufacturing process and during ordinary transportation and handling of the finished product.

In another of its aspects the invention involves new methods of reducing the massive metal to the desired comminute form, and of handling it through all stages of manufacture, transportation and ultimate utilization, with a minimum of hazard heretofore unattained.

Other objects and aims of the invention, will appear in the course of the following description, in which are set forth the characteristics of the products referred to, and the steps of process and the operating conditions employed in the manufacture.

At the present time there are three magnesium powders commonly used for military purposes, known as grades A, B, and C, respectively. Of these, grade A is minus 80 mesh and finer, with a minimum metal content of 93%. Grade B answers the requirement of all particles through a 115 mesh screen, with a minimum of 90% through a 200 mesh screen and a minimum metal content of 92%. Grade C is identified by the fact that a maximum of 12% of the particles are held on a 48 mesh screen, a minimum of 76% pass through a 48 mesh screen but remain on a 100 mesh screen, and a maximum of 12% pass through a 100 mesh screen, with a minimum metal content of 96%. There is also a powder known as "Photoflash," of

which a minimum of 60% passes through a 200 mesh screen, and all of it passes through an 80 mesh screen, with minimum metal content of 95%.

Any means for mechanically removing from the massive metal a usable powder particle, results in the production of a variety of particle sizes. In some instances the intended use of powders so produced allows a considerable range of particle sizes. Where military use is contemplated, grade A, above, is the only grade in this category. If the manufacturer has sufficient diversity of demand for his product so that it is profitable to classify his hetero-sized product, and allocate the fractions so classified among the various grades, he may readily supply the several grades above specified, so far as particle size is concerned. It has been demonstrated that the finer grades, i. e., grade B and Photoflash, result casually during the manufacture of the coarser grade C or of the most hetero-sized material, grade A. It is one of the interesting and important features of the present invention that it makes possible, if desired, the manufacture of the grade B material in quantity but little short of the total starting material, and as the main rather than as the by-product. And another feature is that the proportions of various usable particle sizes in a given mass as the comminuting operation is finished may be to an extent regulatably predetermined; this, of course, has a distinct bearing upon the yield of any particular grade that may be desired.

Manufacture begins with the removal from massive high purity magnesium metal, in ingot, bar, rod, billet, stick or other suitable form, of chips or turnings, as by means of appropriately designed filing machines. The design and/or coarseness of file used produces particles of varying bulking density, with important effect upon the ease with which the various grades of finished powder are produced in subsequent operations.

The material to be filed is fed against the reciprocating file by suitable means, and speed of reciprocation of the file, and pressure of the metal against the file are regulated in view of the desired volume of production and the suitability of the product for the subsequent operations required for the various grades. The filing operation (and this is an important feature of the invention) is conducted under a heavy stream of coolant, e. g., mineral spirit or other high flash petroleum solvent. This "wet filing" operation results in increased production and diminution of hazard as compared with similar operations

conducted under dry conditions; and the liquid-coolant also serves as a vehicle to carry the filed-off particles into a hopper or receptacle, whence they proceed to a so-called disc mill or equivalent device, by means of which many or most of the filed-off particles are reduced in size. A disc mill comprises two relatively rotatable grinding plates operating in a bath of coolant such as already described. The design of the plates, the spacing between them, and the relative speed of rotation determine the degree to which the filed particles are broken along chatter planes and the degree to which the curved particles thus produced are flattened, or even reduced in thickness. These factors are controlled so as to produce a major proportion of material having the descriptive qualities of any one or more of the several grades enumerated above. Following disc milling the magnesium in partial suspension in the coolant is pumpable by standard methods. It is, therefore, lifted to a screen having a mesh suitable to remove oversize particles, these being diverted to another disc mill and after a second milling pumped back into the stream going to the screen. The undersize from this screen is conducted to any standard wet classifying device, such as a wet screen or a wet centrifugal classifier, where the —200 material, i. e., Photoflash, is removed in suspension in the coolant, being caught in hanging filter bags, the coolant passing through the bags and going by gravity to a spirit reservoir for re-use in the filing and/or disc-milling operation.

The material held on the 200 mesh screen or precipitated in the wet classifier is now of a desired size distribution, in accordance with and because of the indicated controls of the filing and disc-milling operations, to answer the requirements of a mixture of (1) grade C, plus (2) grade A, and (3) mill feed for grade B. However, a portion of the —200 mesh material previously screened out will have to be returned (added) to the grade A component.

In any case the material (except the mill feed for grade B) is centrifuged to a definite metal content and then filled into bags, like those just referred to in connection with the separating out of "Photoflash," the bags being of textile material such as what is known as "mole-skin," or "napped twill," with the nap on the inner surface of the bag, substantially dust-tight to the minimum size particles fed into them, but permitting the passage of the coolant and/or coolant fumes, the filtered-out coolant going to a reservoir for re-use. These bags are to hold a measured quantity of material, and are sealed against loss of metal. When the material is wanted in the truly dry state, the sealed bags are brought to a drying compartment, where they are placed upon perforated or expanded metal trays which are electrically connected to a wet ground terminal to prevent the accumulation of static charges.

When all the trays in a compartment are so filled, the compartment is closed and heated air is drawn through the compartment from the outside, and after passing over the moist bagged material is exhausted to the outside air at a place sufficiently removed from the intake to prevent the recirculation through the compartment of air laden with spirit vapors. This is an inefficient drying process, as such, due to the fact that the warm air is not recirculated, which is the practise in other commercial drying installations. In these, even when the liquid which is being re-

moved from the product forms an explosive mixture with the air, recirculation is practised and means are taken to ensure that the vapor concentration is always below the explosive limit. It is preferred, however, to pay the additional cost in size of equipment installed, and amount of steam consumed, so as to be sure that no potential explosive spirit-air mixtures are supplied to the material being dried.

Passage of heated fresh air is continued until the powder contained in the trays is thoroughly dried. When this state is attained the passage of heated air is stopped and the passage of air, at atmospheric temperature, or slightly thereunder, is commenced, until the material contained in the bags is brought to atmospheric temperature. When this condition is attained the cooled, dried, material, still in the closed bags, is placed in appropriate metal containers, in which it is shipped to the consumer.

We have referred to a process for the production of grades A and C magnesium powder in a form more useful to the loaders of pyrotechnic components, to which their use is almost solely confined, than is the dry form now specified by the military establishments that developed the munitions in which they are used. In our process we recognize the necessity, on the part of the users of these grades of powder, to coat the dry powder with oil, usually linseed oil or castor oil, before incorporating them into the other ingredients of the pyrotechnic charge. It is well known that such oils are characterised by their higher surface tension and viscosity, which make them prone to remain in spherical globules when in contact with dry metallic surfaces.

If, however, the metal surfaces to which it is intended or sought to apply a uniform coating of the oil, are first thoroughly wet with a liquid in which that oil is soluble, as happens when material is processed by wet filing and disc-grinding as above set forth, that metal surface so wetted will much more readily receive a uniform coating of the solution of the oil in the same liquid. Subsequent evaporation of the solvent will leave an increasingly concentrated oil-liquid solution until, with the evaporation of the last traces of the solvent, the solute will be uniformly distributed over the surface of the particle which was originally wetted with the solvent liquid.

Thus may be accomplished a more thorough, uniform and satisfactory oil-coating of the metal powder particles than is possible by any attempts to oil-coat metal powder that has either been produced dry, or has been produced wet and subsequently dried. It is contemplated, therefore, to take metal powder that has been comminuted in the presence of a spirit or other suitable non-aqueous coolant while still wet therewith, and either before or during or after the comminution of the metal to add to the spirit the oil with which the metal powder is eventually to be coated. It is preferred to make this addition in the form of a solution of the oil in the spirit after centrifuging or otherwise bringing the comminuted metal to a known spirit content, but it is obvious that the oil could be added at other stages of the process. This point, i. e., after centrifuging and before bagging, is chosen because a definite percentage of oil is usually specified, and the time consumed in removal of the solvent or spirit is lessened by the lessening of the spirit content of the metal before the powder goes to the drying compartment. The control

of the oil content is also more sure by this means.

Powder wet with a solution of oil in spirit, as distinguished from powder wet only with a readily volatile spirit, is relatively non-dusting (and, therefore, not so liable to the hazard of explosion) after the spirit has been evaporated. The drying and packaging of oil-coated powder is less involved, therefore, than the similar operation on uncoated, or pure, powder. In this case, bagging in sealed bags may be unnecessary and the removal of the spirit or solvent may be accomplished in pans having a cover of the aforesaid "mole-skin" cloth, placed in the trays of the drying compartments. Packing entails only the removal of the cover and the scooping up of the solvent-free oil-coated powder into metal containers.

While the advantages of producing a coating on powder by the above means are theoretically obvious, experimental results corroborate these statements; and it has been found that powders coated in this way are more satisfactory from the standpoint of candle power developed during burning, than dry powders subsequently oil coated. The difference observed is shown below:

Coating method	Candle-power developed
The instant process	885,000
Coating of dry powders	850,000

Grade B powder.—This material is 90% —200 mesh of a minimum metallic content of 92% Mg. As previously stated, a process for the manufacture of this product in substantial percentages of the total amount of metal comminuted to obtain it, has long been needed. Three factors have obstructed the high percentage production of this grade. First, is the tendency of magnesium to oxidize readily in presence of oxygen-bearing gases, such as air, water vapor, or CO_2, when its particle size is reduced by cold working. Second, is the tendency of particles of ductile metals to weld together when milled in complete absence of oxygen bearing gases, e. g., in nitrogen. Third, is the greater tendency to formation of explosive metal-air mixtures as the particles decrease in size, when these particles are free to move in the air, i. e., in any dry process. For various reasons, including safety, therefore, a wet ball-milling procedure was developed, in order to produce a powder of the required degree of fineness and metallic content; these factors had to be considered:

(1) The atmosphere of the ball mill.

(2) The degree and rate of cold working produced in the wet ball milling operation. This involves diameter of mill, speed of rotation of the mill, size and weight of balls, etc.

(3) The particle size of the mill feed, with particular attention being paid to the particle thickness.

(4) The composition of the charge, i. e., the ratio of metal to weight of balls and to weight of spirit.

The atmosphere of the ball mill must be such that the available oxygen content in a sealed mill is less than that required for the oxidation of sufficient metal to reduce the metallic content below that specified, i. e., 92%. It appears that under some conditions of wet ball milling, any oxygen present in the combined form, i. e., CO_2, H_2O, etc., is to be considered as substantially all available for the oxidation of the metal, as though

it were in the free molecular state of O_2. Thus, magnesium milled in an atmosphere of CO_2 and N_2 for two hours (impact milling) showed these results.

	Metal	CO_2	N_2
	Percent	*Percent*	*Percent*
Start	99	12	88
Finish (two hours)	91	1	99

It also appears that this utilization of the normally fixed oxygen content of oxides in the oxidation of metals is catalysed by the cold working of the ductile metal in certain zones of the ball milling operations and not in others.

Thus, coarse magnesium of 95% metal content milled at room temperature in a CO_2 or air atmosphere was reduced to all —200 mesh material of 91% metal content in two hours. Yet —200 mesh material of 95% metal content is stable to air if not worked. Even on standing for weeks it shows no significant reduction in metal content. It is believed that the greater chemical activity of the metal while it is being milled is due to the formation of the highly cold-worked "Beilby layers" of metal, which exhibit some of the properties of the liquid phase of the metal in question in being more reactive than unstrained metal. In any event, magnesium can be oxidized in air atmosphere at room temperature when sufficiently severe cold work is done upon the metal particles.

One can grind the same metal particles in the same gaseous atmosphere with reduced oxidation if the grinding is done in the zone of attrition rather than the zone of impact in the ball mill. This is indicated by the fact that —200 mesh material produced by disc-milling in air atmosphere, a typical attrition method, always has a metal content above 95%, whereas all impact ball milled material is below this.

As one would expect, the grinding is less efficient in the former case but also the lower efficiency must be accepted if the metal content is to be held above 92%. It is, therefore, recommended to mill in an atmosphere consisting of a mixture of N_2 and CO_2 and/or O_2 and H_2O held to the specified limits or any combination of them; thus it is recommended that the combined quantities of O_2, H_2O, and CO_2 present in the milling circuit, computed to MgO, $Mg(OH_2)$, and $MgCO_3$, be maintained at not in excess of 8% $MgO+Mg(OH_2)+MgCO_3$, based on the weight of metal charged into the mill, the mill circuit being closed. CO_2 and/or O_2 are necessary ingredients in the mill atmosphere in order for grinding to the required —200 mesh to take place. It is found that increasingly fine grinding takes place with an accompanying increase in oxide content of the powder as the percentage of CO_2, O_2 or H_2O increases, and that as N_2 percentage approaches 100 the tendency for the material to flake rather than grind increases with increasing tendency to retain the original metallic content without oxidation.

For example, coarse magnesium filings milled three hours in nitrogen gave only 8% —200 material. Same type of feed milled three hours in 12% $CO_2+88\%$ N_2 atmosphere gave 78% —200 material. Same type of feed milled three hours in 90% $CO_2+10\%$ nitrogen atmosphere gave 98% —200 material.

It is observed also that the degree of cold working done in the wet ball mill influences the above tendencies materially so that under some atmos-

pheric conditions and of metal content of original mill feed, milling in the range of attrition is necessary in order to preserve the metallic content as specified, under other conditions of mill atmosphere and mill-feed characteristics, impact milling is possible with a preservation of metallic content.

Thus if the original feed used in ball milling for grade B is sufficiently reduced by other methods (filing and/or disc-grinding), methods which do not work the surface enough to induce or promote rapid oxidation, ball milling in the zone of impact will give a very satisfactory product. Thus 100 pounds of feed of 99% plus metal content milled in a 3 ft. diameter x 9 ft. long mill with 5,000 pounds of balls at 47 R. P. M., with 25 gallons of mineral spirits, in an atmosphere of air, mill sealed, temperature 43° C., barometric pressure of 30" Hg gave a 97% yield of grade B material of 93% metal content, density 0.60, flow 10 grams in 90 sec., Metals Disintegrating Company Flow-Tap meter.

Grades A and "Photoflash" can be prepared in a similar way, thus grinding 100 pounds of magnesium under the same conditions as those for grade B, given above, for three and one-half hours gave a 95% yield of "Photoflash" (62% —200 mesh) of 95.5% metal content.

A similar run made with 150 pounds of filed and disc ground metal for two hours gave an 80% yield of grade A of 94% metal content.

Control of particle size range, or the designated grades of material can be achieved by making use of the discovery that comminution of malleable metals can be achieved only in the presence of gases or vapors which react chemically with the metal undergoing comminution. Therefore, the degree to which magnesium metal can be subdivided in a closed ball mill can be controlled either by adjusting the amount of oxygen, carbon dioxide or other reactive gas in the mill atmosphere, or by adjusting the weight of metal charged into the mill when the atmosphere introduced into the mill is one of constant composition such as air. With such control of disintegrating conditions, the amount of subdivision achieved is largely independent of time. Thus in two grinds in which magnesium was milled in a sealed mill in air under identical conditions other than time of grinding one grind of six hours gave an 85% yield of —200 mesh magnesium, another of eighteen hours gave 95% of —200 mesh magnesium. In both grinds the oxygen was completely consumed. Use of this fact, i. e., the dependency of comminution on the metal-charge-and-reactive-gas relation, allows control of degree of comminution or of the designated grades.

Thus in a ball mill 3 ft. in diameter and 9 ft. long, containing 5,000 pounds of balls, air atmosphere sealed in, 100 pounds of magnesium filings and 25 gallons of mineral spirits milled six hours at 47 R. P. M. gave 95% yield of grade B magnesium. Similarly, the same atmosphere, with 150 pounds of magnesium and 33 gallons of spirit gave a 90% yield of "Photoflash" grade; and 200 pounds of magnesium and 50 gallons of spirit gave a 90% yield of grade A.

Although in the production of the grades of magnesium enumerated above, the preferred atmosphere for ball milling is air, where fine and efficient grinding is desired and a low metallic content (say about 85%) can be tolerated, an atmosphere of carbon dioxide will give the best results.

Carbon dioxide, in addition to furnishing the oxygen necessary for comminution of magnesium metal, has the capacity for causing magnesium particles to adhere to the steel balls and mill walls. This armouring effect improves greatly the efficiency of grinding and reduces contamination of the product with iron, etc., from mill balls and walls.

Thus, showing efficiency of CO_2 as grinding atmosphere, consider the following comparison of grinding efficiency and oxidation of metal in milling magnesium in air and carbon dioxide atmospheres, respectively:

Mill_____36" diameter, 6" deep
Balls_____280 lbs., ¼"–⅜"
Feed_____4 lbs., coarse Mg fillings
Vehicle_____1 gal. mineral spirits
Speed_____47 R. P. M.
Temperature_____50° C.

Atmosphere in sealed mill	Time of milling	Yield of —200 Mg. powder in product	Mg-metal in product
	Hours	Percent	Percent
90% N₂+10% CO₂_____	2	75	90
80% N₂+20% O₂ (air)_____	2	19	94
90% CO₂+10% air_____	1	90	88

Some explanation of the technique of ball-milling and of the difference between attrition and impact, between the effects of cascading of balls and cataracting of balls, is set forth in U. S. Patent No. 2,002,891, to Hall.

Where particular materials or forms of apparatus are mentioned in the specification, it is to be understood that materials or apparatus equivalent for the purposes of our invention are contemplated and may be substituted, except where the language of the claims clearly forbids.

And where in the specification it is stated that a certain procedure, involving certain materials, temperatures, etc., is followed, reference is implied to typical examples given in the specification, not as limitative of the claims, but as illustrating the technique to be followed.

We claim:

1. The method of producing comminuted metal of such chemical characteristics and particle size that when dusting thereof occurs in certain atmospheres there is danger of explosion, which consists in subjecting the massive metal to the action of a disintegrator effective to produce and remove from the mass a succession of particles of size within a given range, protecting the particles, as they are produced, by a volatile liquid hydrocarbon coolant, removing coolant and filling the still wet material into a dustproof bag that is pervious to the coolant and to the fumes thereof, sealing the bag, and accomplishing the further removal of coolant.

2. The method of producing comminuted metal of such chemical characteristics and particle size that when dusting thereof occurs in certain atmospheres there is danger of explosion, which consists in subjecting the massive metal to the action of a disintegrator effective to produce and remove from the mass a succession of particles of size within a given range, protecting the particles, as they are produced, by a volatile liquid hydrocarbon coolant, removing coolant and filling the still wet material into a dustproof bag that is pervious to the coolant and to the fumes thereof, sealing the bag, and accomplishing the

further removal of coolant and thereafter drying the bag and its contents by means of moving heated air.

3. The method of producing comminuted metal of such chemical characteristics and particle size that when dusting thereof occurs in certain atmospheres there is danger of explosion, which consists in subjecting the massive metal to the action of a disintegrator effective to produce and remove from the mass a succession of particles 10 of size within a given range, protecting the particles, as they are produced, by a volatile liquid hydrocarbon coolant, removing coolant, adding a solution of oil in coolant liquid, mixing and filling the still wet material into a dust-proof 15 container that is pervious to the coolant and to the fumes thereof, and thereafter substantially completely removing the coolant and leaving the metal particles coated with the oil.

4. A method of producing comminuted mag- 20 nesium and controlling the explosive tendency of said metal which comprises in stated order the steps of subjecting massive metal to the action of an abrader to produce and remove from the mass a succession of particles, mixing said par- 25 ticles as they are produced with a volatile liquid hydrocarbon, transporting said particles in said

hydrocarbon into and through at least one further disintegrating step, draining a portion of the hydrocarbon from the disintegrated particles, charging the remaining hydrocarbon-particle mass into bags pervious to the hydrocarbon and fumes thereof, and thereafter drying the bag and its contents by means of moving heated air.

5. A method of producing comminuted magnesium and controlling the explosive tendency of said metal which comprises in stated order the steps of subjecting massive metal to the action of an abrader to produce and remove from the mass a succession of particles, mixing said particles as they are produced with a volatile liquid hydrocarbon, transporting said particles in said hydrocarbon into and through at least one further disintegrating step, transporting said particles in said hydrocarbon on and through classifying screens, draining a portion of the hydrocarbon from the disintegrated particles, charging the remaining hydrocarbon-particle mass into bags pervious to the hydrocarbon and fumes thereof, and thereafter drying the bag and its contents by means of moving heated air.

                     HAROLD E. HALL.
                     ALEXANDER F. KNOLL.