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TRIAZINE ADDITIVES TO METAL POWDERS

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This invention relates to powder metallurgy. More particularly, it relates to additives for metal powders and still more particularly, it relates to a new class of compounds to be used as additives during the molding or treatment of metal powders.

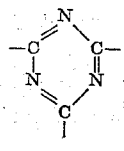
The fabrication of metal parts from metal powders has become increasingly significant on the modern industrial scene. In recent years more and more uses and techniques involving metal powders have been developed. Early development work showed that it was often necessary to utilize an additive of some kind to the metal powders in order that the metal powders might more easily be fabricated into the desired object. These additives may serve as lubricants or as means of imparting desirable properties to the finished metal object. Generally speaking, the lubricant must meet certain requirements.

The class of compounds known commercially as stearates have been widely used as metal powders additives. The stearates have served the role of lubricants well. There has developed, however, an increasing need for a greater variety of lubricants and additives than has heretofore been available. Investigations as to the role of additives have developed the fact that no single additive possesses properties desirable in all applications. It has become more and more apparent that a wider variety of additives should be available in the metal powders industry in order that an additive may be chosen to achieve a specific goal. Instead of classifying an additive as having generally good or bad properties, it has become apparent that an additive should be given a series of ratings with variable coefficients that would depend on the step or steps of the powder metallurgy process considered most important for a given application. For example, certain stearates tend to slow or stop the flow of metal powders in a feed hopper, to lower the transverse rupture strength of the green (unsintered) compact and to be detrimental during sintering. On the other hand, many stearates improve the transmission of pressure in the compacting die, reduce die wear, facilitate ejection, and increase the density of the green compacts.

As a further illustration of the great variety of differences needed in additives, it can be pointed out that in the production of a complicated part, the life of a very expensive die could be the most important element. However, in the automatic production of a simple part in a cheap die, the rapid continuous flow of powder from the feed hopper may be most important.

It is the object of this invention to present a new class of additives useful in powder metallurgy.

To this end the invention contemplates contacting metal powders with a composition comprising at least one compound having the following basic structure:



wherein the unsatisfied valences in the above nucleuses are attached to a member selected from the group consisting of amine, N-substituted amine, hydroxy, oxy, alkyl, and mixtures thereof. The nucleus may also have its valences satisfied by heterocyclic ring containing carbon and nitrogen; compounds such as melon are illustrative of this latter type. Illustrative of the additives contemplated by the present invention are melamine, melamine cyanurate, ammeline, ammelide, ammeline: ammelide compound, melam, melem, melon, cyanuric acid, and guanamines such as stearoguanamine. The chemical structure of these compounds is known. It must be pointed out that the compounds can occur in tautomeric isomers and that the isomers are within the contemplation of the present invention.

It has been discovered that the characteristics of compounds containing the triazine nucleus given above yields the crystal habitat appropriate for additives to metal powders such as copper, copper base alloys, aluminum, iron and the like. At the same time, for any one additive, such physical properties as particle size, shape, and size distribution also affect lubricating characteristics. For this reason, it is preferred that a major proportion of the triazine additives of the present invention be within the size range of about 0.05–15.0 microns and more preferably within the size range 0.1–5.0 microns. The means by which the particle size of the triazine additives may be produced within the desirable limits are well known in the art. Generally speaking, the smaller sized particles of the triazine additives are obtained simply by desubliming the compounds from the vapor phase.

Although all of the triazines described above are useful as additives to metal powders in the molding of the powders, it must be pointed out that the additives do not all enhance the molding process by means of the same mechanism. The different triazines have different desirable properties. Furthermore, it is possible to enhance the overall desirability of the triazines by blending or mixing them either with each other or with other known additives such as the commercial stearate soaps. This is a particularly useful property of the triazine additives since there is such a large number of different steps in the powder metallurgy process, each of which may demand its own additive having properties in conflict with additives demanded by other steps of the process. For example, ammeline and melamine do not affect the flow rate of metal powders; the powders have been blended with small portions of these two additives and have been tested by allowing the metal powders to flow down a standard funnel through a standard hole. Comparisons of the various additives may be made by this system by measuring the amount of metal powder-additive mixture that flows through the hole in any given time. Whereas ammeline and melamine do not affect the flow rate, these two compounds do have the property of increasing the green density of the compact when mixed with the metal powder to the extent of about 0.5%. Furthermore, tests show that melamine increases the density of the green compact better when blended with fine powders than with coarse, whereas ammeline gives better results when blended with coarser metal powders.

The triazine additives have the unusual property when used as an additive to metal powders of evaporating during the sintering of the green compact. They have the unusual property of not possessing a true melting point; thus the sintering of a metal compact using triazines as additives is carried out with more ease than with prior lubricants which first must melt before they can be boiled away.

Stearoguanamine has unusually excellent properties as far as melting point, ejection pressure required to eject the compact from the mold, and the final appearance of

the sintered compact is concerned. Thus, stearoguanamine is one of the best of the all-around additives in respect to the conditions met within the mold.

Cyanuric acid, melamine cyanurate, ammeline, ammelide and the ammeline:ammelide compound are all useful to increase the density of the green compact. In addition there is a marked lowering of the sooty appearance of the sintered compound even when using relatively high percentages of triazine additives as for example as much as 4% by weight of the metal powder. When lower percentages, as for example, 0.5–1.0% of additive are used, then there is no observable marking of the surface of the compact when viewed with the naked eye.

Melam has much the same properties as an additive as does melamine, save the melam has a higher decomposition temperature. This property is advantageous when metal powders are subjected to unusually high pressures as might be the case with a large compact.

Melon has the property of being stable at red heat. As far as a lubricant is concerned, melan has some similarity with graphite. Melan is particularly useful to apply to the interior walls of the molds; this latter method of application may be used in conjunction with or in opposition to admixing the additive with the metal powders. The additive may be dusted on the walls or it may be dissolved or slurried in a solvent such as carbon tetrachloride and sprayed or painted on the interior wall of the mold. Such application greatly reduces the friction between the individual particles of metal powders and the wall of the mold during pressing; this minimizes pressure losses. Although any of the triazine additives may be utilized as a die wall lubricant in this manner, melon is particularly good.

The ammeline:ammelide compound is formed by a union of one molecule each of ammeline and ammelide. The precise structure for the complex is uncertain, but it is known that a bond of some sort does exist between each of the molecules ammeline and ammelide to form the compound. The compound may be prepared by those reactions known to the art which prepare either ameline or ammelide or mixtures of the two.

The triazine additives of the present invention may be utilized in any desired manner. As mentioned earlier, the additives may be dissolved in a solvent and sprayed or painted on the inerior walls of the mold. Alternatively, the additives may be blended in an amount of about 0.25%–5.0% by weight of the metal powder to be employed. One important function of the additive is to serve as a lubricant to facilitate ejection of the pressed part from the die by providing lubrication between the powder and the walls of the molds. Internal lubrication by dispersion of the lubricant through the mass of the powder will mainly serve to minimize the internal friction which will result in less pressure losses. The triazine additives are excellent for the hot pressing processes wherein the compacting and sintering are carried out simultaneously. They also serve to facilitate the extrusion of metal powders.

The melting point of an additive must be high enough to prevent melting at the temperature reached when the powder is subjected to high pressures. If the lubricant melts, it may cause adherence of extraneous powder after compacting and result in a faulty piece on sintering. In this respect, the triazine additives are unusually good. The melting points of the triazine additives are such that there is not any liquification during the period of time when the metal powder is subjected to high pressures.

The ejection pressure is the pressure necessary to eject the compact from the die after pressing. The ejection pressure must be low enough to avoid breaking of the compact. With the exception of stearoguanamine, the ejection pressure of the triazine addities are usually equal to or greater than the ejection pressure obtained when using the prior art additives such as stearate soaps.

However, when ejection pressure becomes an important criterion in the molding of metal powders, as for example, in the molding of an intricate compact which might break under too high an ejection pressure, the triazine additives of the present invention may be blended with either stearoguanamine or the lubricant stearate soaps of the prior art. This blend results in a lowered ejection pressure and a retaining of many of the desirable properties of the triazine additives. A mixture of ammelide and a stearate soap is usually excellent in this respect.

The problem of carbon deposition which takes place in and on the compact in the reducing atmosphere during sintering is very important. Too much soot on the exterior of the piece imparts a dull black appearance. The triazine additives are very good in this respect. Tests show that even as much as 4% of the triazine additives will not destroy the excellent exterior appearance of the compound after sintering.

Exemplary of the type of blending that can be done with the triazine additives of the present invention is a mixture of stearic acid plus ammelide. A half and half blend of stearic acid and ammelide when added to a metal powder to the extent of about 3% results in a molded compact having an excellently low ejection pressure and resulting in an unusually clean and bright surface of the compact after sintering.

The blending of the triazine additives with the metal powders may be carried out in any convenient manner. For example, a mixture of the proper proportions by weight of the additives and the metal powder may be placed in tumbling mill or blending mill of suitable kind and the mixture blended until the suitable degree of mixing has been obtained.

In the practice of the present invention, the symmetrical triazine lubricant is added to the metal powder in either dry form or dissolved in a suitable solvent, such as ether, carbon tetrachloride, alcohol and the like. In general, the dry form is preferably employed although dissolved lubricant can be painted or sprayed on a die surface. Lubricant and metal powder are next mixed completely. The mixture, which will comprise up to about 5% by weight of lubricant and the remainder metal powder, is flowed into a suitable die and is there pressure molded at pressures usually between 5,000 and 75,000 pounds per square inch. The molded article is ejected from the die at pressures substantially less than the compacting pressure. Usually these are in the range of from one-fifteenth to one-twentieth of the formation or compacting pressure. For example, in the prior practice, the use of lubricants such as stearic acid or salts thereof required about 50% or more ejection pressure as compared to the pressure when utilizing the presently described lubricants. The ejected article is next sintered at temperatures ranging from about 300° C. to a few degrees below the temperature of the melting point of the compacted metal or metal alloy. Sintering may take place either in the presence of air, hydrogen or nitrogen. It has been found that temperatures between about 300° C. and 1000° C. or even higher are satisfactory for most sintering operations. The sintered compact upon cooling has good, soot-free appearance.

As previously stated, any metal powder may be employed in the present practice. The powder may be prepared by methods well known in the art, such as atomization, to produce finely divided metal particles.

The invention will be illustrated in conjunction with the following examples which are to be taken as illustrative only and not by way of limitation. Unless otherwise stated, the parts are by weight.

Example 1

A mixture of 99 parts of copper metal powder and 1 part of stearoguanamine lubricant is prepared and introduced into a suitable mold equipped with compacting

and ejection plungers. The average particle size of the lubricant is 0.3 micron. The mixture is then compacted under a pressure of approximately 55,000 p. s. i. by bringing the compact plunger into operation. The pressure is released after impact and the molded article is next ejected from the die under a pressure of about 2750 p. s. i. The ejected article is next placed in a sintering furnace for about 30 minutes at 950° C. The thus-treated article upon cooling is free from soot.

Substituting in separate runs melamine, melamine cyanurate ammelide, ammeline:ammelide compound, melam, melon, melem and cyanuric acid for the lubricant of Example 1 and repeating that example, soot free products are obtained.

Example 2

The process of the previous example is repeated in every material detail except that a mixture of 95 parts of copper powder and 5 parts of stearoguanamine is employed. Although the amount of lubricant is substantially increased, the sintered compact is free from soot. The compact is clean and can be readily machined, as desired.

Example 3

Repeating the process of Example 1 in every respect except that melamine is substituted for the lubricant therein, a valuable soot free compacted article is obtained.

Example 4

Into a suitable mold vertically positioned and equipped with an upper compact plunger and a lower ejection plunger is fed by flowing a mixture of 88 parts of copper powder, 10 parts of tin powder and 2 parts of ammelide of 0.5 micron average particle size. The mixture is compacted under a pressure of approximately 70,000 p. s. i. Upon release of the compacting pressure, the molded article is ejected from the die by the application of an ejection pressure of about 4600 p. s. i. The compact upon ejection is placed in a sintering furnace for about 90 minutes at 750° C. Upon cooling, the compacted alloy is observed as being free from soot, of good tensile strength and machinability.

This application is a continuation-in-part of our copending application, Serial No. 435,920, filed on June 10, 1954, entitled "Triazine Additives to Metal Powders," now abandoned.

We claim:

1. In the method of preparing metallic articles from metal powders which comprises contacting metal powders with an additive, subsequently pressing said powders while in contact with and in the presence of said additive to form a compact, and heating said compact to form a metallic article, the improvement which comprises contacting said metal powders prior to pressing with a triazine additive selected from the group consisting of melamine, melamine cyanurate, ammeline, ammelide, ammeline:ammelide compound, melam, melon, melem, cyanuric acid and stearoguanamine, and wherein said triazine additive is added in an amount equal to about 0.25–5.0% by weight of said metal powder.

2. The method according to claim 1 wherein a major proportion of said triazine additive is in the size range of about 0.05–15.0 microns.

3. The method according to claim 1 wherein a major proportion of said triazine additive is in the size range of about 0.1–0.6 micron.

4. The method according to claim 1 wherein said triazine additive is blended with said metal powder.

5. The method according to claim 1 wherein said triazine additive is spread on the wall of a mold in which said pressing step is carried out.

6. A composition of matter comprising a metal powder and from about 0.25% to about 5.0% of a compound selected from the group consisting of melamine, melamine cyanurate, ammeline, ammeline:ammelide compound, ammelide, melam, melem, melon, cyanuric acid and stearoguanamine.

7. A composition of matter according to claim 6 in which a major portion of the triazine additive is in the size range of about 0.05–15 microns.

No references cited.