Aug. 21, 1962 E. R. BREINING ET AL 3,049,799

METHOD OF GAS PLATING

Filed July 28, 1958 4 Sheets-Sheet 1

Fig-1

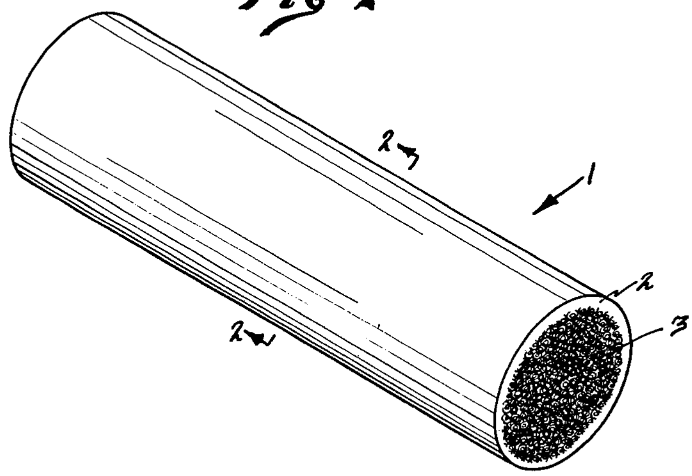


Fig-3

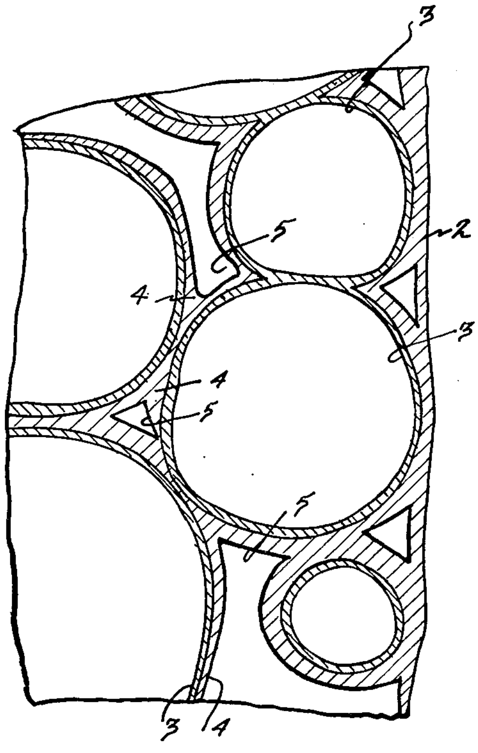
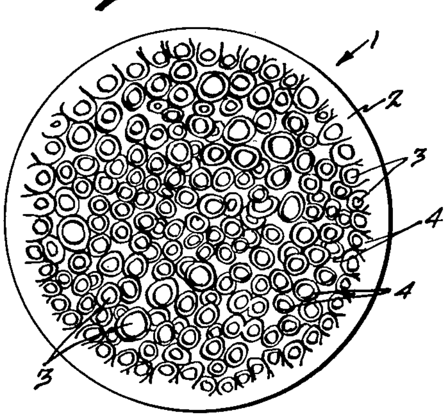


Fig-2



INVENTORS
ELMER ROBERT BREINING
JOHN R. WHITACRE
BY Toulmin & Toulmin
ATTORNEYS

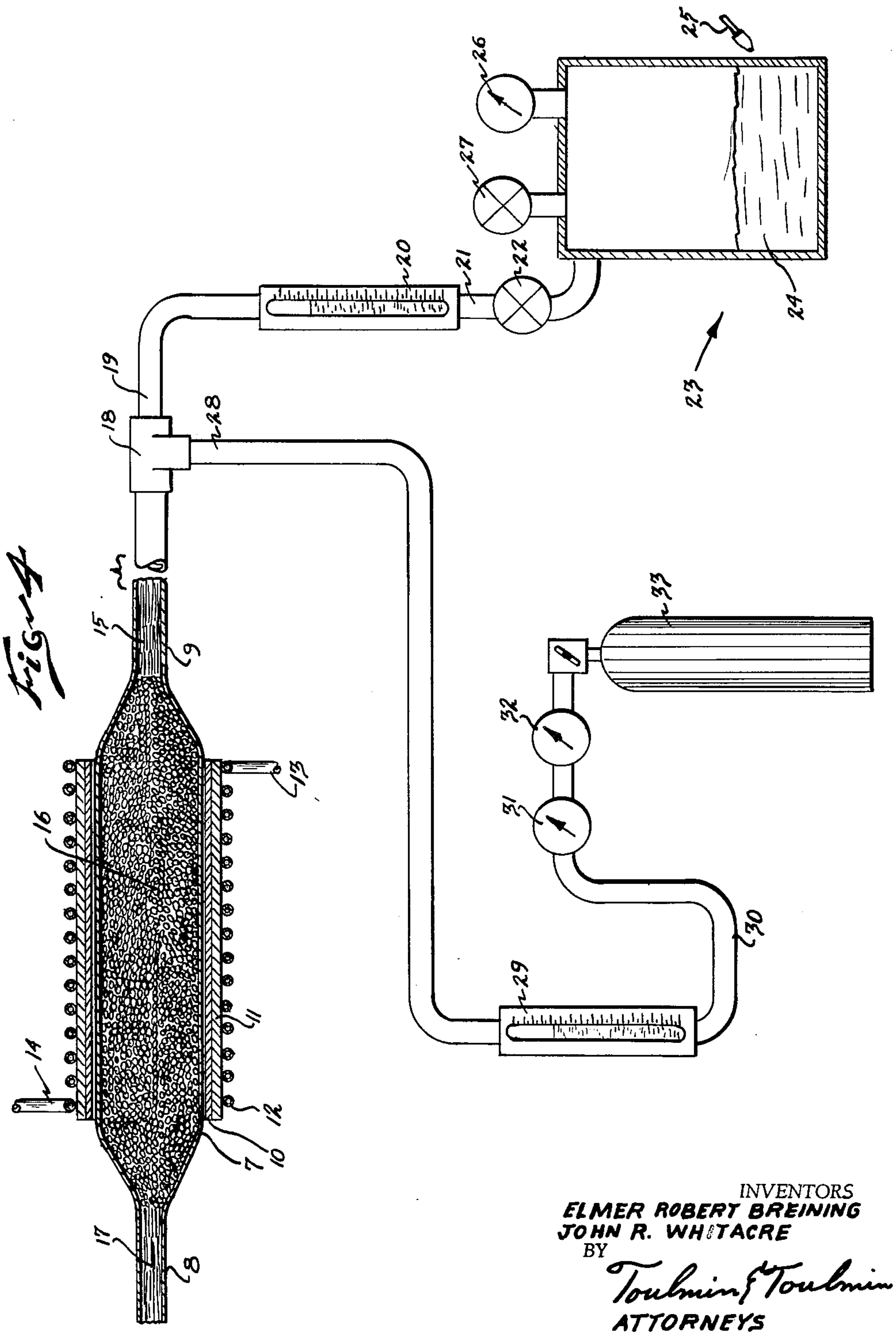


Fig. 4

INVENTORS
ELMER ROBERT BREINING
JOHN R. WHITACRE
BY
Toulmin & Toulmin
ATTORNEYS

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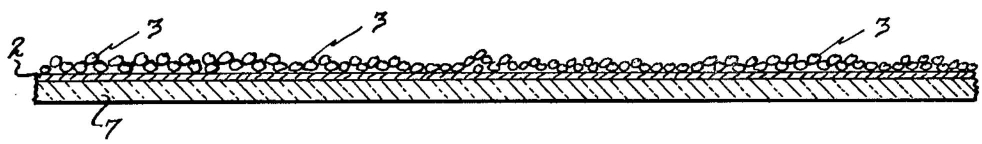
Fig-5



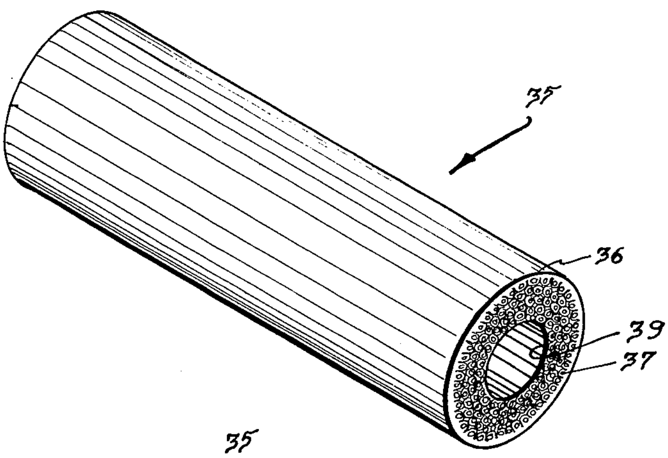


Fig-6

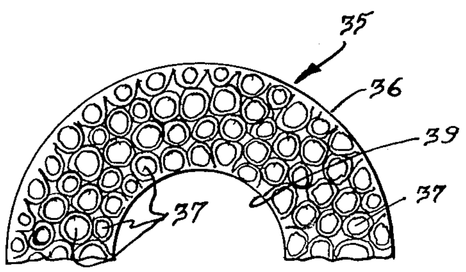
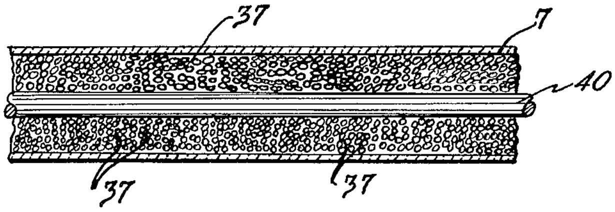


Fig-7

Fig-8



INVENTORS
ELMER ROBERT BREINING
JOHN R. WHITACRE
BY
Toulmin & Toulmin
ATTORNEYS

Fig-9

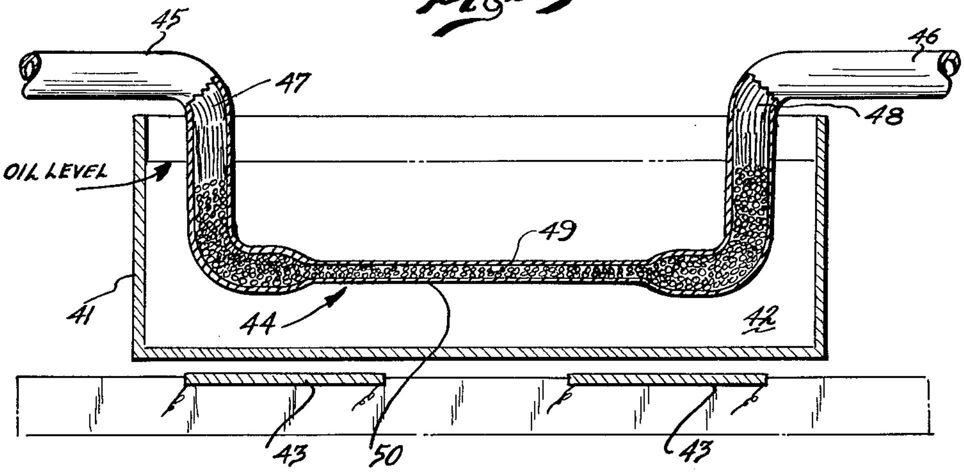


Fig-10

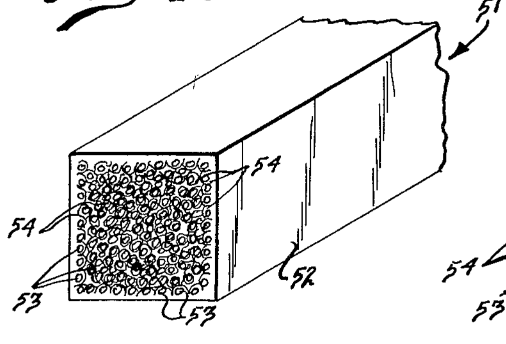


Fig-11

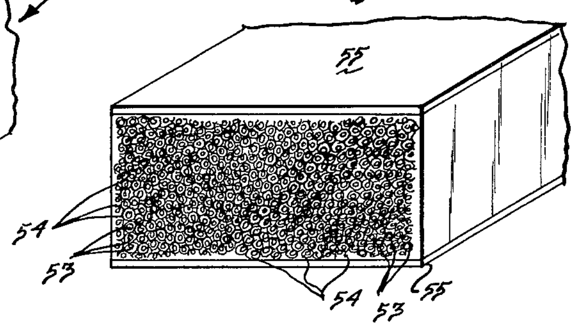
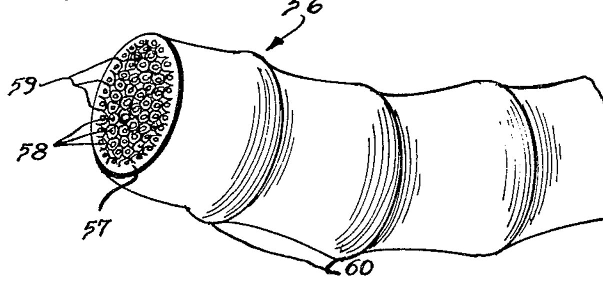


Fig-12



INVENTORS
ELMER ROBERT BREINING
JOHN R. WHITACRE
BY Toulmin & Toulmin
ATTORNEYS

3,049,799
METHOD OF GAS PLATING

Elmer Robert Breining and John R. Whitacre, Dayton, Ohio, assignors, by mesne assignments, to Union Carbide Corporation, New York, N.Y., a corporation of New York

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4 Claims. (Cl. 29—420)

This invention relates to the metallizing of a confined body of individual particles or fragments by gas plating and to articles produced thereby. More particularly the invention relates to the provision within the interstices of a confined body formed by a loose mass of fragments, particles or the like, of metal deposited from heat decomposable gaseous metal bearing compounds, the deposit having as a primary function the formation of a metallic network which extends through the confined body and retains the particles or fragments together.

The invention particularly contemplates a method of providing a gas-plated metal deposit as a network extending through a body of particles, which particles may be hollow or solid, and comprised of glass, metal, clay, the carbides such as silicon carbide, and resin materials, or mixtures of such components. Preferably to secure a high strength to weight ratio in the product the particles are hollow and small—but sufficiently large to permit ready permeation of the interstices, defined by the adjacent particles of the body, by the plating gas.

It is particularly contemplated by the invention to provide a gas plated product which is readily contoured to a predetermined shape, which has a good strength to weight ratio, low elongation and good compression characteristics and which is resistant to corrosive attack.

The invention will be more fully understood by reference to the following detailed description and accompanying drawings wherein:

FIGURE 1 is a perspective view of a gas plated product in accordance with the invention;

FIGURE 2 is a transverse sectional view of the product of FIGURE 1;

FIGURE 3 is a representation of a photomicrograph of a portion of a product such as that illustrated in FIGURES 1 and 2;

FIGURE 4 is a view schematically illustrating apparatus useful in the practice of the method of invention;

FIGURE 5 is a fragmentary view illustrating one phase of the method of invention;

FIGURE 6 is a perspective view of a tubular product illustrating a further modification of the invention;

FIGURE 7 is a transverse sectional view of the product of FIGURE 6;

FIGURE 8 illustrates a step in the formation of the product of FIGURES 6 and 7;

FIGURE 9 is a view illustrating another apparatus set up useful in the practice of the invention;

FIGURE 10 is a perspective view illustrating another modification of the invention in which the shape of the product is substantially rectangular;

FIGURE 11 is a view similar to that of FIGURE 10 but illustrating the product provided with opposing plates; and

FIGURE 12 is a view particularly illustrating a product having various contours formed in accordance with the teachings of the invention.

Referring to the drawings, and first particularly to FIGURES 1–3, inclusive, the numeral **1** generally designates a solid rod having an outer skin **2** and a mass of fragments **3** retained together by metal deposited from the gaseous state and indicated at **4** (FIGURE 3).

The term "fragments" as used herein is intended to indicate particles, pellets, marbles, and so forth, and

shapes which when loosely packed in contacting relation define a body through which interstices exist between the fragments. Such interstices are indicated at **5** in FIGURE 3.

Referring now to FIGURE 4 and the apparatus in which a shaped article, such as that shown in FIGURE 1, is formed, the numeral **7** denotes a glass tube having slightly narrowed end portions **8, 9**. Surrounding the tube in close contacting relationship therewith is a pipe **10**, around which there is wrapped electrical insulating material **11**. Supported on the electrical insulating material **11** is an induction heating winding **12** having leads **13, 14** providing power to the winding.

One narrowed end portion **9** of the tube **7** is provided initially with a mass of glass fibers and the tube is then filled with aggregates indicated at **3**, and which in the present instance may be considered as fine hollow spherulitized clay fibers of about 20 mesh. The tube **7** is suitably substantially completely filled with the clay particles, and then the second end of the tube is closed with a mass of glass fibers **17**.

The tube end **9** is provided with a **T** connector **18** having an inlet **19** from a flow meter **20**. The flow meter **20** is connected through conduit **21** and shut-off valve **22** to a vaporizer indicated generally at **23** and having a supply of liquid carbonyl designated **24**.

A nozzle **25** is arranged to provide a hot air blast over the vaporizer **23** and to create a pressure of nickel carbonyl within the vaporizer. This pressure is indicated by the gauge at **26**; and **27** designates a filling valve for the vaporizer.

The second end of the **T** connector, indicated at **28**, is connected to a flow meter **29**. Flow meter **29** communicates through a conduit **30** with a carbon dioxide cylinder designated **33**, the cylinder itself being provided with a gauge and the pressure reduction valve, the latter being designated at **31, 32**.

Example I

In the practice of the method of the invention in one experiment the vaporizer was brought to a temperature of approximately 100° F., and the gauge then indicated a pressure of about 8 pounds per square inch. The induction heater was turned on and the specimen heated to approximately 350° F. Nickel carbonyl was then introduced at a flow meter of about 9 cubic centimeters per minute in vapor form. Carbon dioxide was flowed through **T**-connector **18** at a rate of about .025 cubic feet per minute. This combined gas stream was then flowed through the tube **7** for a period of about 2¼ hours. At the end of this period the glass tube was removed from the apparatus and the tube broken to procure the specimen, that is, the metallized body.. The gases permeate the interstices and decompose to provide metal on the particles. This metal is substantially in the form of a continuous network extending through the body of the particles.

Initially a deposit of metal is built up as designated at **2** in FIGURE 5 around the inner wall of the tube and between the tube and the body of the loosely packed fragments. This is for the reason that the heat as applied is somewhat greater at the surface of the glass and that the clay particles themselves tend to be poor heat conductors. However, the layer **2** of FIGURE 5, which forms the ultimate skin of the product, as clearly shown in FIGURE 2, facilitates heat conduction. In many instances such a layer may itself be initially formed either by a gas plating procedure or other procedure to aid heat conduction to the fragments themselves.

In the specific experiment to which reference has been made the deposit of metal was about four times the weight of that of the spherules employed. A tensile strength of a specimen, having a diameter of 0.453 inch, was about 14,000 pounds per square inch at an elongation of about 1 percent. A compressive force of 38,000 pounds per square inch reduced the length of the above specimen 56 percent without ruptures.

To procure a more rigid structure compressionwise, more rigid particles, such as silicon carbide, may be used.

The weight of an average sample produced as described above, having a diameter of approximately 0.455 inch, plus or minus 0.003 inch, and a length of about 8 inches, was 5.75 grams per lineal inch. This is comparable to aluminum.

Example II

A specific procedure in the manner described above when heat treated at about 700° F. for 4 hours and then cooled, exhibited a tensile strength of about 9,000 pounds per square inch at an elongation of about 3.3 percent.

As illustrative of the conditions suitable for effecting the above noted procedure of Example I, the following test data are presented:

No.	Temp., ° F.	$NI(CO)_4$, cc./min.	CO_2, c.f.m.	Time, hrs.
1	290	5	.15	.75
2	270	5	.15	2.5
3	270	5	.15	2.5
4	270	5	.15	2.5
5	350	7	.025	2.25
6	380	5	.025	2.3
7	360	9	.2	2.5
8	350	5	.025	2.5
9	320	7	.025	5
10	350	5	.025	2.25
11	{350 2.25 hrs. / 400 30 min.}	9	.025	2.75
12	380	9	.025	1.5
13	400	6	.025	1.5
14	350–400	6	.025	1.5
15	350	6	.025	4
16	350	4	.025	4.5
17	370	4	.025	2.5
18	370	5	.025	2.75
19	370	5	.025	2.75

Referring now to FIGURES 6, 7 and 8, there is shown therein a tubular article and the method of producing it. Referring to FIGURE 6 initially the numeral **35** designates the tubular article generally, while the skin of metal on the outer surface of the body is indicated at **36**. The numeral **37** designates the fragments and the numeral **38** indicates the metal deposited from the gaseous state on to the fragments.

A core opening is indicated at **39**. This core opening is formed as illustrated in FIGURE 8 by providing within the glass tube **7** at the start of the operation an aluminum rod **40** around which the fragments **37** are positioned. The glass tube **7** is then, with the aluminum rod in position, placed in the apparatus as indicated in FIGURE 4 and the metallizing is effected in the same manner.

On completion of the metallizing operation, the cooling of the tube, and the removal of the tube from the apparatus, the aluminum rod **40** is removed from the body. This is suitably effected by first breaking the glass to expose the body itself.

The specimen was then etched in sodium hydroxide, a concentration of about 20 percent at 140° F. until the aluminum tubing was completely etched away.

The exterior skin of the resultant product, designated generally by the numeral **36**, had a fine shiny appearance and a coating of the metal extended over the inner wall bounding the opening **39**.

Rectangular samples or samples of square cross-section may be also produced in accordance with the invention as illustrated in connection with FIGURE 10, wherein **51** generally denotes the structure, **52** indicates the skin around the body, **53** denotes the particles and **54** designates the metal on the particles.

Further such a structure as illustrated in FIGURE 11 at **55** may have plates or other supporting material secured to opposite faces thereof, for example, the opposite faces may be gas plated to provide the relatively thick plates, or in a given instance plates might be attached by welding.

The structures indicated in the preceding figures, that is the FIGURES 1, 6 and 10, may also be produced by the apparatus indicated in FIGURE 9. As shown the numeral **41** designates a container having a quantity of oil **42** filling the container to a suitable level. This container is provided on hot plates **43** in order to effect heating of the oil. A tube **44** having an inlet **45** and an outlet **46** is provided at **47** and **48** at the respective inlets and outlets with a quantity of fiber glass. Particles **49** such as already described fill the narrowed portion **50** of the tube. The tube and the fragments or particles are heated by the oil and the mixture of the nickel carbonyl or other plating gas and carbon dioxide or other inert gas are flowed to the particles through the mass of glass fibers, the decomposed gases flowing to the exhaust at **48**. An interlacing or network of metal is provided over the fragments as previously described. Upon removal from the oil bath the tube **44** is cooled and broken to expose the metallized body of fragments. In this instance also a skin forms around the tube wall and accordingly the metal network and fragments are enclosed by a skin.

The tube already described as container for the fragments may be in any desirable form and if the particles employed are of sufficiently small size they will conform readily to the contour of the container or form. Thus as indicated in FIGURE 12 a very irregular shape may be produced accurately.

In FIGURE 12 the numeral **56** designates a rigid structure having a skin **57**, fragments **58** and metal **59** over the fragments. The numeral **60** designates a contoured outer surface, an accurate reproduction of the form employed.

It is to be noted in connection with the foregoing description that the product of the operation, upon removal from the glass tube, is smooth and is a mirror-like surface. However, it is to be understood that it is not necessary to employ a form of glass, but other forms such as ceramic, hard rubber, or any material which will appropriately withstand the heat, may be utilized.

Also, it is to be noted that the network of metal rigidly bonds together the fragments.

The product is useful in structural as well as ornamental applications, and since its physical characteristics closely approach those of aluminum metal, it may be substituted for aluminum metal in many applications, such as in airplane structure parts.

Attention is also called particularly to FIGURE 3 which is a representation of a photomicrograph of a product as illustrated in FIGURE 1. It is to be noted that not all of the interstices between the spherulitized particles are filled with metal, but that sufficient metal is present to bridge most of the gaps and to create a rigid light weight structure.

In addition to nickel other carbonyls, such as the hexacarbonyls, chromium, and the pentacarbonyls of iron, may be employed in the practice of the invention. Particularly it is to be noted that the gas plated metal, being of a high purity, tends to resist corrosion. Further, where low softening point materials, such as some plastics, are employed the temperature utilized to effect the deposition of the metal, in the case of nickel carbonyl, may be considerably lowered, for example, to about 230° F. Thus, for example, the metallizing of resinous material, such as methyl methacrylate, is practical.

Further, glass spherules, hollow or solid, may be employed to provide a structure having high compression strength and low compressibility.

Where desired metal fragments may form the inner core and the metal might even be of nickel fragments or nickel powder, to provide an integral structure of one metal, but formed with voids as indicated in FIGURE 7 of the drawings.

It will be understood that this invention is suscepti to modification in order to adapt it to different us and conditions and accordingly, it is desired to cor hend such modifications within this invention as may fall within the scope of the appended claims.

What is claimed is:

1. The process which comprises providing a body of loosely packed contacting fragments within a container such that the body takes the shape of said container and the fragments define interstices between themselves, said fragments being hollow, spherulitized and of low heat conductivity, heating the container to thereby transmit heat to the fragments, permeating the body with a heat decomposable metal bearing gas whereby metal deposits from the gas initially at a greater rate on the wall portion of the container than in the body of the fragments to cause further heating of the fragments through the deposited metal, continuing the permeation of the body with the gas to provide a network of deposited metal throughout the body thereby binding the fragments by said deposited metal and inclosing spacings between the fragments, and thereafter removing the container from the metallized body of fragments.

2. The process of binding a mass of solid particles together, which comprises providing a body of loosely packed contacting solid particles within a container and wherein said body takes the shape of said container and the particles define interstices between themselves, said particles being of low heat conductivity, heating the container to thereby transmit heat to said particles, permeating the body with a heat-decomposable metal bearing gas whereby metal deposits from the gas initially at a greater rate on the wall portion of the container than in the body of said particles to cause further heating of the particles through the deposited metal, continuing the permeation of the body with the gas to provide a network of deposited metal throughout the body thereby binding the particles by said deposited metal and inclosing spacings between the particles, and thereafter removing the container from the metallized body of particles.

3. The process of binding a mass of solid particles together, which comprises providing a body of loosely packed contacting solid particles within a container and wherein said body takes the shape of said container and the particles define interstices between themselves, said particles being hollow and of low heat conductivity, heating the container to thereby transmit heat to said particles, permeating the body with a heat-decomposable metal bearing gas whereby metal deposits from the gas initially

at a greater rate on the wall portion of the container than in the body of the said particles to cause further heating of the particles through the deposited metal, continuing the permeation of the body with the gas to provide a network of deposited metal throughout the body thereby binding the particles by said deposited metal and inclosing spacings between the particles, and thereafter removing the container.

4. The process of binding a mass of solid particles together, which comprises providing a body of loosely packed contacting solid particles within a container and wherein said body takes the shape of said container and the particles define interstices between themselves, said particles being of low heat conductivity, heating the container to thereby transmit heat to said particles, permeating the body with a heat-decomposable metal bearing gas whereby metal deposits from the gas initially at a greater rate on the wall portion of the container than in the body of said particles to cause further heating of the particles through the deposited metal, continuing the permeation of the body with the gas to provide a network of deposited metal throughout the body thereby binding the particles by said deposited metal and inclosing spacings between the particles, and thereafter removing the container from the metallized body of particles, said body of particles being heated to a temperature of between about 270–400° F. for permeating the body with heat-decomposable metal bearing gas.

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