United States Patent

Brushek et al.

[15] **3,650,715**

[45] **Mar. 21, 1972**

[54] **ABRASIVE COMPOSITIONS**

[72] Inventors: **Dieter Klaus Brushek; Frank Clyde Starr, Jr.**, both of Wilmington, Del.

[73] Assignee: **E. I. du Pont de Nemours and Company**, Wilmington, Del.

[22] Filed: **Apr. 4, 1969**

[21] Appl. No.: **813,754**

[52] **U.S. Cl.** **51/298,** 51/295, 51/309

[51] **Int. Cl.** **C08g 51/12,** C09c 1/68

[58] **Field of Search** 51/298, 295, 309

[56] **References Cited**

UNITED STATES PATENTS

3,295,940 1/1967 Gerow 51/298

3,518,068 6/1970 Gillis 51/298

Primary Examiner—Donald J. Arnold

Attorney—Claude L. Beaudoin

[57] **ABSTRACT**

Abrasive compositions and articles such as grinding wheels and hones formed therefrom which abrasive compositions contain from 6 to 35 volume percent of diamonds from 5 to 65 volume per cent of a dendritic form of a metal such as copper, or silver or alloys thereof, from 10 to 75 volume percent of a coalesced aromatic polyimide and up to 80 volume percent (but retaining the 10 volume percent minimum of polyimide) of the polyimide phase of a filler or a metal coating on the diamonds.

11 Claims, No Drawings

ABRASIVE COMPOSITIONS

BACKGROUND OF THE INVENTION

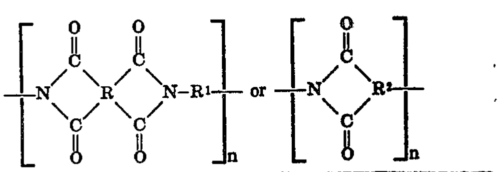
In the past polyimide bonded diamond grinding wheels have been produced containing various combinations of diamond fillers and polyimide fillers. Generally, these grinding wheels have exhibited grinding properties superior to other diamond grinding wheels for wet grinding materials such as tungsten carbide and the various cemented carbides but not for dry grinding these materials. It is believed that these high loadings of metal filler serve among other functions to conduct away heat as it is generated by the grinding operation. Previously the problems involved in fabricating polyimide resin powders made high loadings of metal difficult to achieve while still maintaining adequate strength in the final product.

SUMMARY OF THE INVENTION

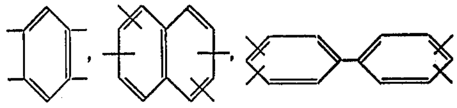
It has now been found that when a particulate dendritic metal filler is incorporated in aromatic polyimide bonded abrasive articles such as grinding wheels or hones an unexpected sharp increase in the dry grinding efficiency or dry grinding ratio of the grinding wheel is obtained. This increase is particularly large when high loadings such as over 40 volume percent of the non-diamond phase of such dendritic metal as compared with other fillers are used.

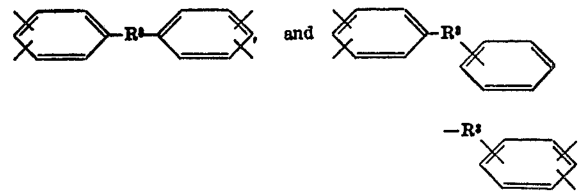
Dendritic metal as used herein refers to an arborescent, branched, tree-like-shaped form which can be prepared electrolytically. Typically, the clusters of dendritic metal particles are from 50 to 600 U.S. Standard mesh size. The individual dendrites within a cluster typically resemble small diameter cylindrical rods, the surface of which is closely covered with branches about 3 microns long and 1 micron in diameter as seen in scanning electron micrographs. The metals which are suitable for use in the present invention are those structural metals which can be electrodeposited in dendritic form and include nickel, iron, zinc, nickel alloys, copper, silver and copper alloys such as bronze and brass. The nature of these dendritic metal particles appears to aid in producing a strong molded object by permitting interlocking of the particles with each other and around the diamonds and resin. The malleability of a metal such as copper permits deformation during the pressing and molding of the resin such that strong molded objects can be produced with relatively low levels of resin binder, a result which is in striking contrast to that obtained with low levers of resin and similar levels of hard or relatively smooth surfaced filler. Thus, diamond abrasive composition made with the dendritic metal-polyimide system at high metal loading can withstand the high forces involved in dry grinding and at the same time easily remove the heat generated by the grinding process from the area surrounding the diamond. The latter permits greater retention of the diamonds with consequent increases in grinding efficiency.

The polyimides used herein are powders of the aromatic polyimides. Generally, these aromatic polyimides have the fomula

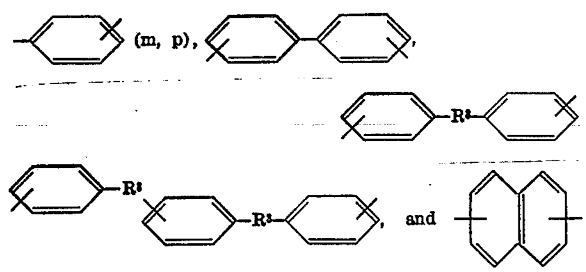


where R, R^1 and R^2 are organic radicals selected from the group consisting of aromatic, aromatic heterocyclic, bridged aromatic and substituted groups thereof. Preferred R's include

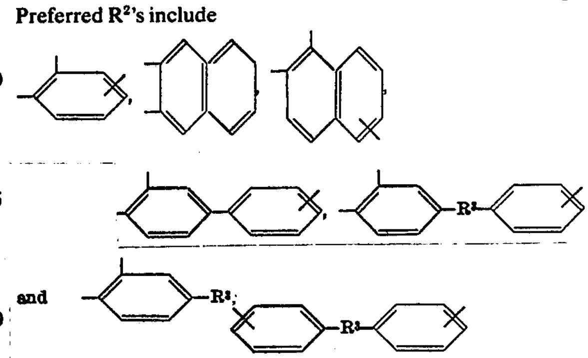




wherein the bonds to the carbonyl groups are arranged in pairs with the carbonyl groups of each pair on adjacent or peri carbon atoms. Preferred R^1's include



When pyromellitic dianhydride is used at least 14 mole percent of the diamine used should contain two aromatic rings. Preferred R^2's include



wherein the bonds to the carbonyl groups are arranged in pairs on adjacent or peri carbon atoms.

R^3 is selected from the group consisting of carbon in an alkylene group or perfluorinated alkylene group of from one to three carbon atoms, oxygen, silicon in

—Si(R^4)$_2$—, —O—Si(R^4)$_2$—O—, —C(=O)—, —C(=O)—NH— phosphorous in

—P(R^4)(=O)—, and —O—P(R^4)(=O)—O—, —NR_5, —S— and —S(=O)$_2$—,

where R^4 is lower alkyl or aryl and R^5 is R^4 or hydrogen. The polyimide powder may be prepared in accordance with the teachings of U.S. Pat. No. 3,249,588 issued May 3, 1966 to Walter George Gall and should have a surface area of at least 0.1 square meter/gram and preferably greater than 2 square meters/gram, as measured by adsorption of nitrogen from a gas stream of nitrogen and helium at liquid nitrogen temperature, using the technique described by F. M. Nelsen and F. T. Eggertson (Anal. Chem. 30, 1387 (1958)). Sample weights are in the order of 0.1–3.5 g. The thermal conductivity detector is maintained at 40° C. and the flow rate is approximately 50 ml./min. The gas mixture used is 10 parts by weight nitrogen and 90 parts by weight helium.

The polyimide should have an inherent viscosity of at least 0.1 and preferably from 0.3 to 5, as measured at 35° C from a 0.5 percent by weight solution in 96 percent sulfuric acid. If the polyimide is not soluble to the extent of 0.5 percent in 96 percent sulfuric acid at 35° C. and a strong article can be coalesced therefrom it is assumed to have an inherent viscosity of greater than 0.1.

The molded abrasive composition generally contains from 6 to 35 volume percent diamonds, from 5 to 65 volume percent dendritic metal, and from 10 to 75 volume percent aromatic polyimide. Optionally, part of the resin phase can be replaced with up to 80 volume percent of another abrasive such as silicon carbide, or aluminum oxide, or a filler such as glass, or a metal in the form of metal coating on the diamonds, powder or metal fibers provided that at least 10 volume percent of the composition is aromatic polyimide. As used herein volume percent is based on the as-molded composition. Generally, the diamonds are from 50 to 300 U.S. Standard screen series size for grinding wheels while diamonds as fine as 1,200 sieve size are suitable for hones.

Generally, when fabricating grinding wheels, the diamond-containing composition is made up as a rim with the diamonds embedded in a coalesced polyimide matrix which rim is then mounted on a core. The core preferably is aluminum, but other materials such as aluminum filled phenolic resin may be used. Hones of various shapes can be molded by similar techniques.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Grinding Ratio Test - I

A D11V9 (American Standards Association) flaring cup wheel is mounted on the spindle of a Cincinnati No. 2 grinder and rotated at 4,000 r.p.m. The work consists of 16 blocks of cemented carbide, grade C-3 or C-5, mounted and evenly spaced on a rotatable head and each having an exposed rectangular surface ¼ inch × ¾ inch. The blocks are ground sequentially by passing the work across the face of the grinding wheel at a table speed of 6 ft./min., returning the work in a spark-out pass and then rotating the head to expose the next block to action of the wheel. When each block has been ground in turn, the work is fed into the wheel 0.002 inch and the grinding cycle is repeated. The whole operation is carried out automatically under dry grinding conditions to remove carbide at a rate of 0.232 in.^{3}/hr. The grinding ratio (GR) is the ratio of the volume of carbide removed to the volume of wheel removed.

Grinding Ratio Test - II

A D11V9 flaring cup wheel is mounted on the spindle of a Gallmeyer and Livingstone No. 28 grinder and rotated at 4,000 r.p.m. The work consists of a row of 6 blocks of cemented carbide, C-2 grade, and 6 blocks of cemented carbide, C-5 grade, each ¼ inch × ¾ inch and spaced alternately 1 inch apart. The table speed is either 2 or 5 ft./min. and the infeed is 0.002 inch. The grinding operation consists of a cutting pass during which each block is ground followed by a spark-out pass prior to the next infeed. The grinding operation is continued at carbide removal rate of 0.14 in.^{3}/hr. and 0.35 in.^{3}/hr. at table speed of 2 ft./min. and 5 ft./min., respectively. The grinding ratio (GR) is the ratio of the volume of carbide removed to the volume of wheel removed.

EXAMPLES 1–3

Examples 1–3 employed 3¾ inches D11V9 flaring cup wheels made from synthetic diamonds, poly-N,N'(4,4'-oxydiphenylene) pyromellitimide binder, and selected fillers. The diamonds were 180 grit, metal clad diamonds present at a 100 concentration (72 carats/in.^{3}) in rims ⅛ inch wide. Grinding ratio test I was used to evaluate the wheels and the results are shown in Table I. The results show that the presence of metal fillers is beneficial with the results using dendritic copper filler unexpectedly good.

TABLE I

Example	Rim composition (vol. percent)				Grinding ratio	
	Diamond	Metal cladding	Resin binder	Filler	C-5	C-3
1	25	12	63	0	4.5	13
2	25	12	33	30 (B-153 brass powder)[a]	11	65
3	25	12	33	30 (dendritic copper)[b]	80	~950

[a] B-153 is 60 mesh 75.7% copper, 19.3% zinc, and 1.4% lead alloy blended with 3.5% iron.

[b] The dendritic copper used here and in Examples 7-14, 18, 19, 21, and 22 was made up of electrolytically produced particles which resemble small diameter cylindrical rods from which small branches protrude. The branches essentially cover the surface of the rod, or trunk, and all are inclined in an orderly fashion at an angle of about 45° to the trunk. Measurement of a typical individual particle showed it to be about 50 microns long with branches about 3 microns long and about 1 micron in diameter. The overall diameter of the particles was about 3 microns. The particles were in a form 99% of which pass through a 100 U.S. Standard sieve. This copper is commercially available under the tradename D-100 Fernlock Copper ® from Malone Metal Powders, Inc.

EXAMPLES 4–9

Examples 4–9 employed 5 inch D11V9 flaring cup wheels made from synthetic diamonds, poly-N,N'(4,4'-oxydiphenylene)-pyromellitimide binder and selected fillers. The diamonds were 150 or 180 grit, optionally metal clad, present at a concentration of 100, 75 or 50 in rims ⅛ inch wide. Grinding ratio test II was used to evaluate the wheels and the results are shown in Table II. The results again show the superiority of dendritic copper filler.

TABLE II

Example	Rim composition (vol. percent)				Grinding ratio at table speed	
	Diamond	Metal cladding	Resin binder	Filler	2 ft./min.	5 ft./min.
4	[a] 25	0	55	20 (copper fibers)	63	24
5	[b] 25	0	45	30 (600 grit SiC)	31	6
6	[b] 25	0	40	35 (Coarse Cu powder)	29	15
7	[a] 25	12	33	30 (Dendritic copper)	380	98.4
8	[a] 18.75	9.25	38	34 (Dendritic copper)	235	54
9	[a] 12.50	6.50	42	39 (Dendritic copper)	156	30

[a] 150 grit (140-170 screen size).

[b] 180 grit (170-200 screen size).

EXAMPLE 10

A 3-¾-inch D11V9 flaring cup wheel was made with the composition of Example 8 except the resin binder used was the polyimide from 4,4'-oxydianiline and 3,3',4,4'-benzophenone tetracarboxylic dianhydride. Under Grinding

Test I conditions using cemented grade C-5, the wheel had a grinding ratio of 49.

EXAMPLES 11–14

Examples 11–14 employed 3-¾-inch D11V9 flaring cup wheels identical to that used in Example 3 except the amounts of resin binder and dendritic copper filler were varied to provide bonds of different degrees of hardness. The results, shown in Table III were obtained using grinding ratio test I.

TABLE III

Rim Composition (Vol. %)

Example	Diamond	Metal cladding	Resin binder	Dendritic copper	Grinding Ratio C–5	Grinding Ratio C–3
11	25	12	53	10	8	65
12	25	12	43	20	11	≈202
13	25	12	23	40	16	521
14	25	12	33	30	39	832

EXAMPLES 15–20

Examples 15–20 indicate the remarkable increase in the strength of compositions containing dendritic metal filler compared with usual copper and silicon carbide fillers (Table IV), when using the polyimide of Example 1.

TABLE IV

Ex.	Composition (vol. percent) Binder	Filler	Flexural strength,[a] p.s.i. (unsintered)	Tensile strength,[b] p.s.i. (sintered)
15	100	0	6,930	11,700
16	75	25 (copper molding powder passes 100 mesh).	1,180	2,420
17	75	25 (SiC 120 grit)	4,340	6,080
18	75	25 (dendritic copper)	7,730	10,050
19	0	100 (dendritic copper)	11,040	----------
20	0	100 (copper molding powder)	([c])	----------

[a] Flexural strength was measured using a 1" span on standard American Powder Metallurgy Institute tensile bars following the procedure of ASTM D-790. Bars were compacted at 100,000 p.s.i. at ambient temperature.

[b] Tensile strength measured using standard American Powder Metallurgy Institute tensile bars following the procedure of ASTM D-1708. Bars were compacted at 100,000 p.s.i. at ambient temperature and free sintered using a heating cycle of twelve hours at 300° C., and 10 minutes at 435° in an oven having a nitrogen atmosphere.

[c] Too weak to be tested.

EXAMPLE 21

Two compositions were prepared by dry blending (a) 40.3 g. nickel clad diamonds (60–80 grit U.S. mesh), 92.0 g. dendritic copper powder and 3.8 g. poly-N,N'(4,4'-oxydiphenylene)pyromellitimide resin, and (b) 72.9 g. dendritic copper powder and 30.1 g. poly-N,N'(4,4'-oxydiphenylene pyromellitimide resin leveled in the cavity of a 3.5-inch diameter cylindrical mold and preformed at ambient temperature and 6,000 p.s.i. Composition (b) was placed and leveled on top of the preformed composition (a) and also preformed at 6,000 p.s.i. The mold and contents were then heated at low contact pressure to 450° C. and the preform was molded at this temperature for 20 minutes under a pressure of 55,000 p.s.i. The mold was cooled to below 200 °C. The pressure was released and the molded cylinder was ejected. The composition of the abrasive layer, as expressed in volume percent, was 25 percent diamond (100 concentration), 50 percent dendritic copper, 13 percent polyimide resin, and 12 percent nickel (cladding on diamonds), while that of the nonabrasive layer was 79.5 percent dendritic copper and 20.5 percent polyimide resin. Hones were cut from the molding 1⅛ inches × ¾ inch and the surface of the abrasive layer, ⅛ inch in depth was machined to a 2-inch radius of curvature in the direction of the short dimension. The yield was 6 hones per cylinder. The bases of 8 hones were shaped to fit the holders of a two-turret honing machine manufactured by Micromatic Hone Corp. for honing cast iron brake drums. After mounting the hones, semi-finished drums of 12 inches I.D. and 2.8 inches width were then honed, during which operation the turrets were rotated at about 170 r.p.m. At equilibrium, the wear ratio, expressed as number of drums honed per gram of diamond consumed was about 1.900. Phenolic bonded stones with the same diamond grit size and concentration exhibited a wear ratio of about 450 drums per gram of diamond used, while the metal bonded stones normally used to hone cast iron brake drums had ratios about the same as that of the composition of this Example.

EXAMPLE 22

An abrasive composition was prepared by dry blending 1.18 g. nickel clad diamonds (60–80 grit, U.S. mesh), 0.10 g. poly-N.N'(4,4'Φ¼-oxydiphenylene) pyromellitimide, 1.3 g. dendritic copper powder, 0.69 g. fine zinc powder and 0.22 g. silicon carbide (400 grit U.S. mesh), and the mixture was compacted in a 1¼-inch diameter cylindrical mold at ambient temperature and 6,000 p.s.i. Dendritic copper powder (17.1 g.) was then compacted on top of the abrasive-containing preform at 6,000 p.s.i. and the mold and its contents were heated to 450° C. under low contact pressure. The preform was molded at this temperature for 20 minutes at 30,000 p.s.i. and cooled under pressure to below 200° C. The resultant disc had an abrasive layer 0.030 inch thick and its composition by volume nickel (cladding on the diamonds), 11.5 percent polyimide resin, 24 percent dendritic copper, 16 percent zinc and 11.5 percent silicon carbide. The high volume loading of fillers with corresponding low volume of resin was made possible by the dendritic nature of the copper filler. The molded composition was shown to be strong and useful by the following test.

The 1¼-inch diameter disc was center drilled to form a 9/32 inch hole and it was mounted on a variable speed, vertical spindle in such a way that the abrasive surface was in contact with a ¼ inch thick cast iron, wear plate having a ring shape whose inside diameter of about 1 inch and outside diameter of about 1¼ inches resulted in an area of contact of 0.4 inch^2. The surface of the wear plate was lapped with a 600 G SiC finish. The flat surfaces of both the test specimen and the wear plate were parallel and in the same plane. The wear plate was thermally insulated from its holder and was connected to a strain gage through a lever arm. A force sufficient to produce a load of 18 pounds on the nominal area of contact of 0.40 inch^2 was applied through the lever arm to the test specimen. The spindle was rotated at a speed such that the velocity of the surface of the test specimen in contact with the wear plate was 600 ft./min., thus giving a PV value (pressure in lbs./in.^{2} × velocity in ft./min.) of about 27,000. After a short break-in period, a wear ratio was calculated following a test of about 1 minute duration using the losses in weight of the wear plate and of the specimen. The result, expressed as grams of cast iron removed per gram of hone material consumed, was 24.0 and the removal rate of the cast iron was 0.012 g./min. The load was increased to give a pressure of 250 p.s.i. at the same velocity (PV=150,000) and the test was carried out for about ½ minute. The wear ratio was again 24.0 but the removal rate had increased about 80-fold to 0.93 g./min. When the same composition was tested by honing cast iron brake drums, as described in Example 21, the wear ration was 1,950 drums honed per gram of diamond consumed.

We claim:

1. An abrasive article comprising from between about 6 and about 35 volume percent of diamonds, from between about 10 and about 75 volume percent of poly-N,N'(4,4'-oxydiphenylene) pyromellitimide, and from between about 5 and about 65 volume percent of compacted dendritic copper.

2. An abrasive article comprising from between about 6 and about 35 volume percent of diamonds from between about 10

and about 75 volume percent of an aromatic polyimide derived from 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 4,4'-oxydianiline, and from between about 5 and about 65 volume percent of compacted dendritic copper.

3. The article of claim 2 wherein said compacted dendritic metal is derived from clustered dendritic particles wherein said clusters are of between about 50 and about 600 U.S. Standard mesh size.

4. An abrasive composition comprising diamonds, coalesceable aromatic polyimide of poly-N,N'(4,4'-oxydiphenylene)pyromellitimide and dendritic copper having in molded form from about 6 to about 35 volume percent of diamonds, from about 10 to about 75 volume percent of said aromatic polyimide, and from about 5 to about 65 volume percent of compacted dendritic copper.

5. An abrasive composition comprising diamonds, coalesceable aromatic polyimide derived from 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 4,4'-oxydianiline and dendritic copper having in molded form from

about 6 to about 35 volume percent of diamonds, from about 10 to about 75 volume percent of said aromatic polyimide, and from about 5 to about 65 volume percent of compacted dendritic copper.

6. The article of claim 1 wherein said compacted dendritic copper is derived from clustered dendritic particles wherein said clusters are of between about 50 and about 600 U.S. Standard mesh size.

7. The article of claim 1 in the form of a grinding wheel.

8. The article of claim 1 in the form of a hone.

9. The article of claim 2 in the form of a grinding wheel.

10. The article of claim 2 in the form of a hone.

11. The composition of claim 4 wherein said dendritic copper is in the form of clustered dendritic particles wherein said clusters are of between about 50 and about 600 U.S. Standard mesh size.

* * * * *