United States Patent Office 2,980,633 Patented Apr. 18, 1961

2,980,633

CARBON AND GRAPHITE ARTICLES

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No Drawing. Filed Mar. 5, 1957, Ser. No. 643,913

8 Claims. (Cl. 252—507)

This invention relates to mixtures of comminuted carbonaceous materials and pitch binders, and to shaped articles produced therefrom.

In the conventional manufacture of carbon articles, comminuted carbonaceous materials such as coke, carbon black and/or artificial graphite are blended with a relatively high melting point coal tar or pitch binder to form what is referred to as a "green" mix. In such a mix the ratio of binder to solid is about 1 to 3. To improve the extrusion characteristics of the mix, a small amount of summer oil, about 4 parts per 100 parts of mix, is usually added. After extrusion, the finished carbon article is obtained by baking to carbonize the binder. The carbon article may be graphitized, if desired, by further heat treatments.

During the heat treatments to which the "green" mix is subjected, a considerable quantity of volatile matter is evolved from the binder and summer oil. As a result, the finished articles, particularly large-sized, fine-grained, graphitic articles, are marred by fissures and voids.

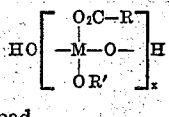
It has occurred to many researchers to reduce the amount of binder and summer oil in the mix to avoid such flaws. To obtain a satisfactory improvement in the quality of the shaped articles, this reduction must be such that the green mix is almost impossible to extrude. There is, therefore, a need for a means of reducing the binder level and/or eliminate the need for summer oil in carbonaceous mixes, which means will not affect the extrusion characteristics of the mix.

The main object of this invention, therefore, is to provide additives which will permit considerable reduction of binder level in carbonaceous green mixes, and will eliminate the need for using summer oil therein.

It is an equally important object of the invention to provide carbon and graphite articles having improved quality owing to the presence therein of certain organo-metallic derivatives.

These and other objects of this invention are achieved by incorporating with green mixes comprising comminuted carbonaceous particles and pitch binders, from 0.1 percent to 5 percent by weight thereof of at least one of the following organo-metallic compounds.

(*a*) Metal carboxylates



M is silicon, tin or lead

R is an alkyl group or substituted alkyl group, having from 10 to 18 carbon atoms

R′ is an alkyl group having from 1 to 4 carbon atoms

x is a small whole number, ranging from 1 to 3.

(*b*) Aminoalcohol derivatives of the formulae:

$$(RO)_xM(OC_2H_4N(R^1)_2)_{4-x}$$

and

$$(RO)_xM(OC_2H_4N(R^1)_2)_{4-x}\cdot Y(HO_2CR'')$$

M is silicon, tin, lead or zirconium

R is an alkyl group having from 1 to 4 carbon atoms

R^1 is an alkyl or substituted alkyl group having from 1 to 4 carbons

R″ is an alkyl group or substituted alkyl group having from 10 to 18 carbons

x is 0 to 3

Y is a number $0 \leq Y \leq (4-x)$

(*c*) Polyhydric alcohol derivatives

$$(RO)_xM(O—Y—(OH)_z)_{4-x}$$

M is silicon, tin, lead or zirconium

R is an alkyl group having from 1 to 4 carbon atoms

Y is a substituted alkylene group, aromatic group, hydroester group, having from 2 to 8 carbons

z is a small whole number ranging from 1 to 3 and

x is a small whole number ranging from 1 to 3.

These compounds, and methods of preparing the same, are disclosed and claimed in our copending applications Serial No. 578,782, filed April 16, 1956, and Serial No. 629,797, filed December 21, 1956.

Illustrative of the successful practice of the invention, test mixes were prepared having the following composition:

(*a*) Control mix containing no additive

1600 grams of coke

560 grams of 30 medium pitch having a melting point around 130°

(*b*) Additive mixes

1600 grams of coke

554 grams of 30 medium pitch binder

6 grams of additive

In the additive-containing mixes the additive content was 1 percent of the pitch weight. The mixes were prepared by weighing the coke and pitch, placing them in covered containers, and heating for one hour at 325° F. (162° C.). The hot coke pitch and additive were placed in a pre-heated mixer, and mixed one hour at 150° C. to 160° C. The mixes were removed from the mixer and allowed to cool. Examination of the respective mixes at this stage indicated that the mixes containing the additives had a much larger aggregate size, were darker and glossier in appearance than the control mix. Of more importance, the mixes containing the additives of the invention were wetter in appearance than the control. To show the effectiveness of the additives of the invention in lowering the binder content, mixes were prepared as indicated above, but having the following composition:

(*c*) High solids mix containing additive

2000 grams of coke

554 grams of 30 medium pitch having a melting point around 130° C.

12 grams of additive.

The combined effect of summer oil and of the additives of the invention was examined by preparing mixes with the following composition:

(*d*) Additive-oil mix

1600 grams of coke

554 grams of 30 medium pitch

6 grams of additive

32 grams of oil.

These mixes contained the same amounts of pitch and additive as the additive mixes described previously, plus two parts of summer oil per 100 parts of coke. The ad-

ditives tested and the code abbreviations used therefor are:

SSTA—Isopropoxy stearoxy polysilicate

SNSTA—Butoxy stearoxy polystannate

In the following tests, all the sample mixes were preheated to 110° C. and extruded at 105° C. through an 0.75 inch die. The extrusion rates and pressure are tabulated in Table I.

TABLE I

The extrusion rates and pressures for various mixes [1]

Additive [2]	Gauge Pressure (lbs./in.²)	Rate (in./sec.)
SSTA	650	1
SNSTA	600	1
SNSTA-0 [3]	280	1
SNSTA-2 [4]	650	1
Control [5]	1,100	0.003

[1] All the mixtures contain coke flour; 30 medium pitch (34 parts pitch/100 flour). The mixes were prepared by mixing the ingredients in a blender at 150° C. for one hour.

[2] All additives are present in an amount of 0.3 gram additive/100 grams of coke.

[3] Two grams of summer oil/100 grams of coke was the quantity of summer oil added to the mix.

[4] This series of rods contains 27.5 grams of pitch/100 grams of coke.

[5] The control contained no additives.

Generally the control mixes were too dry to measure their extrusion pressures and rates accurately; the data for the control mixes in Table I are, therefore, approximations.

The effect of summer oil in conjunctions with the additives of the invention is to decrease extrusion pressures required by 50 percent over those for the additive mixes, the high solid mix extruded at nearly the same pressure and rate as the regular additive mixes. None of the extruded rods except the control rods showed fissures on visual observation, and all had a smooth surface of high luster, indicative of a good quality product.

Table II shows the densities of the green rods; with the exception of the high solids mix, all fall within the range of 1.62 to 1.67 grams per cc. In the case of the high solids mix, which exhibited a density of 1.58 grams per cc., apparently there was not enough pitch to fill all the voids in the coke.

CALCINATION OF EXTRUDED SHAPES

The sample rods extruded as indicated above next were calcined at 1000° C., and subsequently graphitized at 3000° C. After each operation the rods were measured, weighed, and their respective densities calculated. As indicated in Table III below, the densities of the calcined rods containing the additives of the invention consistently fell in the range of 1.48 to 1.56, which densities are in the correct range for good calcined stock.

TABLE II

Dimensions and properties of the green test rods

Dimensions	SNSTA-2 [1]	SNSTA [2]	SNSTA-0 [3]	SSTA-1 [2]	SSTA-2 [2]
Weight (grams)	68.39	71.68	71.70	72.48	72.29
Diameter (inches)	0.768	0.770	0.768	0.770	0.770
	0.768	0.768	0.766	0.769	0.770
	0.766	0.764	0.765	0.770	0.767
	0.768	0.770	0.768	0.770	0.772
	0.767	0.767	0.767	0.771	0.771
Avg. Diameter (inches)	0.766	0.764	0.764	0.771	0.767
Length (inches)	0.767	0.767	0.766	0.770	0.770
Volume (cm.³)	5.792	5.772	5.767	5.773	5.771
Density (g./cm.³)	43.85	43.70	43.55	44.05	44.04
	1.582	1.644	1.646	1.645	1.641

[1] These series of rods contain 27.5 parts of pitch/100 flour and 0.5% additive, based on total weight of the mix, and were made from a high solids type of mix as mix (*c*) of page 5.

[2] All these additives are present in an amount of 0.3% by weight of the total mix, and were made from type (*b*) mixes.

[3] These series of rods contain summer oil present in to the extent of 2% of the weight of the coke, and were made from type (*d*) mixes.

TABLE III

Dimensions and properties of test rods calcined at 1000° C.

Dimensions	SNSTA-2 [1]	SNSTA [2]	SNSTA-0 [3]	SSTA-1 [2]	SSTA-2 [2]
Weight (grams)	61.98	65.11	63.33	64.58	64.78
Diameter (inches)	0.756	0.759	0.761	0.758	0.761
	0.753	0.756	0.758	0.758	0.760
	0.753	0.750	0.753	0.758	0.758
	0.755	0.761	0.761	0.759	0.760
	0.754	0.756	0.759	0.759	0.760
Avg. Diameter (inches)	0.752	0.752	0.755	0.758	0.758
Length (inches)	0.754	0.766	0.766	0.758	0.760
Volume (cm.³)	5.728	5.709	5.754	5.731	5.710
Density (g./cm.³)	41.91	43.06	43.45	42.38	42.44
	1.479	1.512	1.458	1.524	1.526

[1] These series of rods contained 27.5 parts of pitch/100 flour and 0.5 g. additive/100 g. of mix, and were made from mix type (*c*).

[2] These series of rods contained 34 parts of pitch/100 flour and 0.3 g. additive/100 g. of mix (type *b*).

[3] These series of rods contained 34 parts of pitch/100 flour, 2 g. summer oil/100 g. flour, and 0.3 g. additive/100 g. of mix (type *d*).

The densities for rods graphitized at 3000° C. as indicated in Table IV were again comparable to densities expected of good specimens.

TABLE IV

Dimensions and properties of test rods graphitized at 3000° C.

Dimensions	SNSTA-2[1]	SNSTA[2]	SNSTA-0[3]	SSTA-1[2]	SSTA-2[2]
Weight (grams)	60.27	63.30	61.52	62.93	62.74
Diameter (inches)	0.746	0.748	0.753	0.751	0.753
	0.746	0.752	0.753	0.753	0.753
	0.746	0.748	0.753	0.755	0.752
	0.747	0.747	0.753	0.753	0.754
	0.747	0.752	0.753	0.753	0.753
	0.746	0.748	0.753	0.753	0.753
Avg. Diameter (inches)	0.746	0.749	0.753	0.753	0.753
Volume (cm.^{3})	40.97	41.14	41.96	41.65	41.76
Length (inches)	5.720	5.689	5.750	5.707	5.722
Density (g./cm.^{3})	1.47	1.54	1.47	1.51	1.50

[1] These series of rods contained 27.5 parts of pitch/100 flour, 0.5 part additive/100 mix (type *c*).
[2] These series of rods contained 34 parts pitch/100 flour, 0.3 part additive/100 mix (type *b*).
[3] These series of rods contained 34 parts pitch/100 flour, two parts summer oil/100 flour, 0.3 part addtive/100 mix (type *d*).

The foregoing data indicates that no deleterious effect as regards the density or appearance of calcined and graphitic shapes accomapny the use of the additives of the invention to reduce the extrusion pressures and binder level content of green mixes.

Graphitized rods above produced were tested for their coefficient of thermal expansion and electrical resistance. These tests are very important in the determination of electrode quality. As indicated in Table V below, the coefficients of thermal expansion and the electrical resistivities of the samples all fall in the useable ranges of 0.151 to 0.159×10^{-5} inches per inch per ° C., and 363 to 400 micro amps per inch square, respectively.

TABLE V

Electrical resistivity of coefficients of thermal expansion of test rods graphitized at 3000° C.

Property	SNSTA-2[1]	SNSTA[2]	SNSTA-0[3]	SSTA-1[2]	SSTA-2[2]
Micro-amps	5.25	3.30	3.74	3.56	3.51
Resistivity (μamps./in.^{2})	574	363	416	396	391
Coefficient of Thermal Expansion (in./in./° C.$\times10^{-5}$)	0.159	0.156	0.157	0.155	0.151

[1] These series of rods contain 27.5 parts pitch/100 flour, 0.5 part additive/100 mix (type *c*).
[2] These series of rods contain 34 parts pitch/100 flour, 0.3 part additive/100 mix (type *b*).
[3] These series of rods contain 34 parts pitch/100 flour, two parts summer oil/100 flour, 0.3 part additive/100 mix (type *d*).

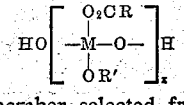
While for the sake of brevity the invention has been described mainly by reference to isopropoxy stearoxy polysilicate and butoxy stearoxy polystannate, the same is not to be construed as limited thereto, but rather to contemplate the use therein of many other compounds comprehended within the definition and formulae given above, including, for example, butoxy stearoxy polysilicate, isopropoxy stearoxy polysilicate, isopropoxy perfluorobutyryl polysilicate, isopropoxy perfluoroacetoxy polysilicate, isopropoxy stearoxy polystannate, isopropoxy oleoxy polystannate, isopropoxy 9,10-dibromostearoxy polysilicate, isopropoxy benzoxy polysilicate, methyl perfluorobutyryl polysilicate, butoxy oleoxy polysilicate, diethoxy-di-(triethanolamine)-silicate, dibutoxy-di-(triethanolamine)-silicate, diisopropoxy-di-(triethanolamine)-silicate, diethoxy-di-(β-diethylaminoethoxy)-silicate, diethoxy-di-(triethanolamine)-plumbate, diethoxy-di-(triethanolamine)-stannate, diethoxy-di-(triethanolamine)-silicate-N-oleate, diethoxy-di-(triethanolamine)-silicate-N,N-dioleate, diisopropoxy-di-(triethanolamine)-silicate-N-oleate, diisopropoxy-di-(triethanolamine)-silicate-N,N-dioleate, dibutoxy-di-(β-diethylaminoethoxy)-silicate-N-oleate, diethoxy-di-(triethanolamine)-plumbate-N,N-dioleate, tetra(triethanolamine)-silicate, diethoxy-di-(triisopropanolamine)-silicate, diethoxy-di-(triisopropanolamine)-silicate-N-oleate, tetra-(2-ethylhexanediol-1,3)-silicate, isopropoxy-tri-(2-ethylhexanediol)-silicate, diisopropoxy-di-(2-ethylhexanediol-1,3)-silicate, diisopropoxy-di-(2-ethylhexanediol-1,3)-stannate, di-(triethoxysiloxy)-glyceryl oleate, tri-(triethoxysiloxy)-pentaerythrityl oleate.

It has been found that the additives of the invention are effective in a large variety of mixes, such as fine grain mixes, large particle mixes and sulfur-containing mixes. In the case of mixes containing relatively large comminuted carbonaceous particles, however, best results are obtained when the additives of the invention are added after 80 percent of the mixing time has elapsed.

The compounds of the invention are effective in mixes containing binders other than pitch. Thus coke mixes containing tar and synthetic resinous binders extruded readily, and produced higher quality extruded stock when 0.3 percent to 0.4 percent of additive was present than in the absence thereof.

What is claimed is:

1. A process for producing shaped carbonaceous articles, which comprises mixing finely divided carbonaceous particles with an organic binder, and from 0.1 percent to 5 percent by weight of at least one additive selected from the group consisting of the carboxylates of tin, silicon and lead, the aminoalcohol and polyhydric alcohol derivatives of tin, lead, silicon and zirconium and mixtures thereof, and forming the resulting mixture into predeterminate shape, said carboxylates having the formula:



wherein R is a member selected from the group consisting of the alkyl, and the substituted alkyl radicals having from 10 to 18 carbon atoms, M is a metal selected from the group consisting of silicon, tin and lead, R′ is an alkyl group having from 1 to 4 carbon atoms, and x is a small whole number ranging from 1 to 3;

said amino alcohols having the formula:

$$(RO)_xM(O{-}C_2H_4N(R')_2)_{4-x}.Y(HO_2CR'')$$

wherein M is a metal selected from the group consisting

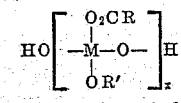
of silicon, tin, lead and zirconium, R is an alkyl group having from 1 to 4 carbon atoms, R′ is selected from the group consisting of the alkyl and substituted alkyl groups having from 1 to 4 carbon atoms, R″ is a member selected from the group consisting of the alkyl and substituted alkyl groups having from 10 to 18 carbon atoms, x is a number ranging from 0 to 3; Y is a number equal to $(4-x)$, and said polyhydric alcoholates having the formula:

$$(RO)_xM[OY-(OH)_z]_{4-x}$$

wherein M is a metal selected from the group consisting of silicon, tin, lead and zirconium, R is an alkyl group having from 1 to 4 carbon atoms, Y is a substituted alkylene radical having from 2 to 8 carbons, z is a number ranging from 1 to 3 and x is a number ranging from 1 to 3.

2. The process of claim 1, wherein said carbonaceous particles are relatively large and said additive is added after about 80 percent of the mixing time has elapsed.

3. A process for producing shaped baked carbon articles, comprising comingling carbonaceous particles with a pitch binder, adding summer oil to the resulting mix, and from 0.1 percent to 5 percent by weight of an additive selected from the group consisting of the carboxylates of tin, lead and silicon, the aminoalcohols and polyhydric alcohol derivatives of tin, lead, silicon and zirconium, shaping the resulting mix and baking to carbonize said binder, said carboxylates having the formula:



wherein R is a member selected from the group consisting of the alkyl, and the substituted alkyl radicals having from 10 to 18 carbon atoms, M is a metal selected from the group consisting of silicon, tin and lead, R′ is an alkyl group having from 1 to 4 carbon atoms, and x is a small whole number ranging from 1 to 3;

said amino alcohols having the formula:

$$(RO)_xM(O-C_2H_4N(R')_2)_{4-x}.Y(HO_2CR'')$$

wherein M is a metal selected from the group consisting of silicon, tin, lead and zirconium, R is an alkyl group having from 1 to 4 carbon atoms, R′ is selected from the group consisting of the alkyl and substituted alkyl groups having from 1 to 4 carbon atoms, R″ is a member selected from the group consisting of the alkyl and substituted alkyl groups having from 10 to 18 carbon atoms, x is a number ranging from 0 to 3; Y is a number equal to $(4-x)$, and said polyhydric alcoholates having the formula:

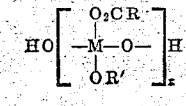
$$(RO)_xM[OY-(OH)_z]_{4-x}$$

wherein M is a metal selected from the group consisting of silicon, tin, lead and zirconium, R is an alkyl group having from 1 to 4 carbon atoms, Y is a substituted alkylene radical having from 2 to 8 carbons, z is a number ranging from 1 to 3 and x is a number ranging from 1 to 3.

4. The process of claim 3 wherein the amount of said additive is at least 0.3 percent by weight of said mix.

5. The process of claim 3 wherein the amount of said additive is at least 0.5 percent by weight of said mix.

6. A green carbonaceous mix characterized by low extrusion pressures, said mix containing carbonaceous particles, an organic binder and from 0.1 percent to 5 percent by weight of at least one additive selected from the group consisting of the carboxylates of tin, lead and silicon, the amino and polyhydric alcohol derivatives of tin, lead, silicon and zirconium and mixtures thereof, said carboxylates having the formula:



wherein R is a member selected from the group consisting of the alkyl, and the substituted alkyl radicals having from 10 to 18 carbon atoms, M is a metal selected from the group consisting of silicon, tin and lead, R′ is an alkyl group having from 1 to 4 carbon atoms, and x is a small whole number ranging from 1 to 3;

said amino alcohols having the formula:

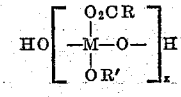
$$(RO)_xM(O-C_2H_4N(R')_2)_{4-x}.Y(HO_2CR'')$$

wherein M is a metal selected from the group consisting of silicon, tin, lead and zirconium, R is an alkyl group having from 1 to 4 carbon atoms, R′ is selected from the group consisting of the alkyl and substituted alkyl groups having from 1 to 4 carbon atoms, R″ is a member selected from the group consisting of the alkyl and substituted alkyl groups having from 10 to 18 carbon atoms, x is a number ranging from 0 to 3; Y is a number equal to $(4-x)$, and said polyhydric alcoholates having the formula:

$$(RO)_xM[OY-(OH)_z]_{4-x}$$

wherein M is a metal selected from the group consisting of silicon, tin, lead and zirconium, R is an alkyl group having from 1 to 4 carbon atoms, Y is a substituted alkylene radical having from 2 to 8 carbons, z is a number ranging from 1 to 3 and x is a number ranging from 1 to 3.

7. A green carbonaceous mix characterized by low extrusion pressures, said mix containing carbonaceous particles, an organic binder, summer oil, and from 0.1 percent to 5 percent by weight of at least one additive selected from the group consisting of the carboxylates of tin, lead and silicon, the amino and polyhydric alcohol derivatives of tin, lead, silicon and zirconium and mixtures thereof, said carboxylates having the formula:



wherein R is a member selected from the group consisting of the alkyl, and the substituted alkyl radicals having from 10 to 18 carbon atoms, M is a metal selected from the group consisting of silicon, tin and lead, R′ is an alkyl group having from 1 to 4 carbon atoms, and x is a small whole number ranging from 1 to 3;

said amino alcohols having the formula:

$$(RO)_xM(O-C_2H_4N(R')_2)_{4-x}.Y(HO_2CR'')$$

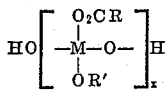
wherein M is a metal selected from the group consisting of silicon, tin, lead and zirconium, R is an alkyl group having from 1 to 4 carbon atoms, R′ is selected from the group consisting of the alkyl and substituted alkyl groups having from 1 to 4 carbon atoms, R″ is a member selected from the group consisting of the alkyl and substituted alkyl groups having from 10 to 18 carbon atoms, x is a number ranging from 0 to 3; Y is a number equal to $(4-x)$, and said polyhydric alcoholates having the formula:

$$(RO)_xM[OY-(OH)_z]_{4-x}$$

wherein M is a metal selected from the group consisting of silicon, tin, lead and zirconium, R is an alkyl group having from 1 to 4 carbon atoms, Y is a substituted alkylene radical having from 2 to 8 carbons, z is a number ranging from 1 to 3 and x is a number ranging from 1 to 3.

8. A green carbonaceous mix characterized by low extrusion pressures and improved forming characteristics, said mix containing cominuted carbonaceous particles, an organic binder selected from the group consisting of tar and synthetic resins, and at least 0.3 percent by weight of mix of an additive selected from the group consisting of the carboxylates of tin, lead and silicon, the aminoalcohol and polyhydric alcohol derivatives of tin, lead,

silicon and zirconium, said carboxylates having the formula:



wherein R is a member selected from the group consisting of the alkyl, and the substituted alkyl radicals having from 10 to 18 carbon atoms, M is a metal selected from the group consisting of silicon, tin and lead, R′ is an alkyl group having from 1 to 4 carbon atoms, and x is a small whole number ranging from 1 to 3;

said amino alcohols having the formula:

$$(RO)_xM(O—C_2H_4N(R')_2)_{4-x}\cdot Y(HO_2CR'')$$

wherein M is a metal selected from the group consisting of silicon, tin, lead and zirconium, R is an alkyl group having from 1 to 4 carbon atoms, R′ is selected from the group consisting of the alkyl and substituted alkyl groups

having from 1 to 4 carbon atoms, R″ is a member selected from the group consisting of the alkyl and substituted alkyl groups having from 10 to 18 carbon atoms, x is a number ranging from 0 to 3; Y is a number equal to $(4-x)$, and said polyhydric alcoholates having the formula:

$$(RO)_xM[OY—(OH)_z]_{4-x}$$

wherein M is a metal selected from the group consisting of silicon, tin, lead and zirconium, R is an alkyl group having from 1 to 4 carbon atoms, Y is a substituted alkylene radical having from 2 to 8 carbons, z is a number ranging from 1 to 3 and x is a number ranging from 1 to 3.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,980,633 April 18, 1961

James O. Koehler et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 5, for "conjunctions" read -- conjunction --; columns 5 and 6, TABLE V, in the heading thereof, line 1, for "of", in italics, first occurrence, read -- and --, in italics; same columns 5 and 6, in the footnotes to TABLE V, the footnote numbered "3" should appear as footnote number -- 2 --; same TABLE V, the footnote numbered "2" should appear as footnote number -- 3 --; column 7, line 21, for "comingling" read -- commingling --; column 8, line 70, for "cominuted" read -- comminuted --.

Signed and sealed this 10th day of October 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents

USCOMM-DC