



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C09K 3/14, B24D 3/28	A1	(11) International Publication Number: WO 93/17080 (43) International Publication Date: 2 September 1993 (02.09.93)
(21) International Application Number: PCT/US93/00551 (22) International Filing Date: 19 January 1993 (19.01.93) (30) Priority data: 07/839,132 20 February 1992 (20.02.92) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventors: HELMIN, Harvey, J. ; HARMER, Walter, L. ; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: WENDT, Jeffrey, L. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).		(81) Designated States: AU, BR, CA, JP, KP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: COATABLE MIXTURES INCLUDING ERODABLE FILLER AGGLOMERATES, METHODS OF PREPARING SAME, ABRASIVE ARTICLES INCORPORATING CURED VERSIONS OF SAME, AND METHODS OF MAKING SAID ARTICLES (57) Abstract <p>Previously known methods of rendering binders erodable do not afford the desired degree of erodability. Coatable mixtures including erodable filler agglomerates, and abrasive articles into which they may be incorporated are presented, the agglomerates comprising a plurality of individual grains of water insoluble filler agglomerated by an agglomerating agent which includes water soluble filler and a binder. A preferred water soluble filler is $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{-}18\text{H}_2\text{O}$, a preferred water insoluble filler is Na_3AlF_6 (cryolite), while a preferred binder is a phenolic resin. The agglomerates may be formed <i>in situ</i> in a binder precursor composition.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LJ	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TG	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

- 1 -

**COATABLE MIXTURES INCLUDING ERODABLE FILLER
AGGLOMERATES, METHODS OF PREPARING SAME, ABRASIVE
ARTICLES INCORPORATING CURED VERSIONS OF SAME,
AND METHODS OF MAKING SAID ARTICLES**

5

This invention pertains to coatable mixtures including erodable filler agglomerates, and abrasive articles incorporating cured versions of same. The erodable filler agglomerates, in one preferred form, comprise cryolite particles and aluminum sulfate. The abrasive articles can be coated abrasives, nonwoven
10 abrasives or bonded abrasives.

Abrasive articles generally comprise abrasive grains secured within a binder. In the case of a bonded abrasive, the binder serves to bond the abrasive grains together such that they form a shaped mass. Typically, this shaped mass is in the form of a wheel and thus it is commonly referred to as a grinding wheel.
15 In the case of coated abrasives, the binder serves to bond the abrasive grains to a substrate or backing, and the binder may be comprised of make and size coatings. In the case of nonwoven abrasives, the binder serves to bond the abrasive grains to a lofty, open, fibrous substrate.

In many abrasive articles the binder includes a particulate filler. Typically,
20 the binder will comprise between 40 to 70 percent by weight particulate filler. The addition of the filler either increases the toughness and hardness of the binder and/or reduces the cost of the finished article, e.g., by decreasing the amount of binder required.

There exists a subclass of fillers, referred to as grinding aids, cutting aids,
25 or generically as "active fillers". An active filler is typically a particulate material the addition of which to the binder has a significant affect on the chemical and physical processes of abrading which leads to improved performance.

In general, active fillers are most efficient when used in a dry grinding mode. The mechanism of wet grinding is much different than dry grinding.
30 Active fillers such as cryolite (Na_3AlF_6) generally do not function as effectively in the wet grinding mode. For equivalent amounts of stock removal, grinding may

SUBSTITUTE SHEET

- 2 -

be done at increasingly higher forces, eventually leading to dulling of the abrasive article through degradation of the binder and/or abrasive grain pullouts. Abrasive product dulling may also occur as a result of the abrasive grains being worn to the make coating level.

5 Thus, an unmet need exists in the abrasives art, particularly in the art of wet grinding, for an active filler that provides for a controlled erosion of the abrasive layer during grinding, which results in a continuous exposure of the working abrasive grains, a slower increase in the required grinding force, and prolonged life of the abrasive article.

10 While the erodable agglomerates of U.S. Pat. No. 5,078,753 has been found to be quite useful in the production of abrasive articles, they do not provide a controllable mechanism to degrade under wet grinding conditions, and their production involves the energy and labor intensive steps of crushing and screening to achieve the desired agglomerate size distribution. It would therefore be
15 desirable to avoid these steps and provide an agglomerate that erodes both under mechanical forces and under wet grinding conditions.

Other references of interest describing the use of cryolite, inorganic sulfates, and the like, as fillers in abrasive articles include U.S. Pat. Nos. 2,016,892; 2,308,982; 4,253,850; 4,311,489; 4,381,188; 4,475,926; 4,609,381;
20 4,761,163; 4,903,440; and 4,907,376, and European Patent Application 0 061 035 A2 (published September 29, 1982). However, none of these references teaches or suggests the production or use of erodable filler agglomerates.

In accordance with the present invention, a coatable mixture including erodable filler agglomerates, and abrasive articles incorporating cured versions of
25 same, are presented. The abrasive articles exhibit improved abrading efficiency when compared with abrasive articles containing only non-agglomerated fillers. During wet grinding operations, a water soluble portion of the erodable filler agglomerates of the invention gradually dissolves, providing a mechanism for the degradation of the erodable filler agglomerates. This leads to an increase in
30 the abrasive layer porosity at the surface and provides a mechanism for erosion of the abrasive layer, thus exposing new abrasive particles.

SUBSTITUTE SHEET

- 3 -

The coatable mixture of the present invention includes erodable filler agglomerates and a binder precursor, the erodable filler agglomerates characterized by being a plurality of individual particles of water insoluble filler agglomerated by an agglomerating agent. "Agglomerating agent", in the case of a coatable
5 mixture in accordance with the invention, is a composition which consists essentially of water soluble filler and binder precursor. In the case of abrasive articles, "agglomerating agent" is a composition which consists essentially of water soluble filler and binder, "binder" meaning a cured resin. The erodable filler agglomerates may thus contain additives which do not adversely affect the
10 erodability of the agglomerates.

As used herein the term "erodable" refers to the ability of an erodable filler agglomerate according to the invention to break down its structure in a controlled manner, for example, by fracture under mechanical grinding forces and/or by the dissolving of a water soluble component under wet grinding conditions.

15 "Water soluble" and "water insoluble" are, of course, relative terms, with solubility of a solute in water generally increasing with temperature. The terms are meant to describe the relative water solubility of the two filler components by their published solubility values in water at 0 - 50°C, as per Table A, below. Thus, "water soluble filler" means an inorganic material having a cold water
20 solubility of at least 10 grams per 100 cubic centimeters (gms/100 cc) water, more preferably at least 50 gms/100 cc of water. "Water insoluble filler" means an inorganic material having cold water solubility of at most 1 gm/100 cc water.

"Water", when used herein in the context of "water solubility" and water as an ingredient in solutions and coatable mixtures, means "consisting essentially
25 of water". "Wet" means grinding conditions where a water spray or flood is used.

"Agglomerating agents consisting essentially of water soluble filler and binder precursor", as used herein, means the water soluble filler is preferably no more than 10 weight percent (more preferably no more than 5 weight percent) of the total weight of water soluble and water insoluble fillers, but at least 10 weight
30 percent (more preferably at least 50 weight percent) of the total weight of the agglomerating agent. The agglomerating agent may comprise binder precursor and

- 4 -

other ingredients, such as non-agglomerated filler, which do not adversely affect the erodability of the erodable filler agglomerates of the present invention. It is theorized that the presence of the water insoluble filler in the coatable mixtures of the invention allows the erodable filler agglomerates to form with much less binder precursor in the agglomerates than the agglomerates of assignee's copending applications, mentioned previously.

The water insoluble filler of the erodable filler agglomerates of the present invention preferably is a material selected from the group consisting essentially of inorganic halide salts represented by general formula I



having a solubility in cold water of at most 10 gms/100 cc and mixtures thereof wherein:

A = alkali metal ion, ammonium ion or combinations thereof;

IIIa = Al^{3+} , Ga^{3+} , or combination thereof;

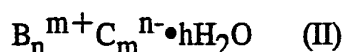
X = halide ion or combination thereof;

y = an integer from 1 to 10; and

z = y + 3.

Particularly preferred water insoluble fillers within formula I include those inorganic halide salts wherein A is an alkali metal ion, most preferably Na^+ ion. It is to be considered within the scope of this invention to include compounds such as $Li_3Na_3(AlF_6)_2$ as water insoluble fillers.

The erodable filler agglomerates of the invention preferably include water soluble fillers selected from the group consisting essentially of inorganic compounds represented by general formula II



having water solubility in cold water of at least 10 gms/100 cc and mixtures thereof wherein:

B = Al, NH_4 , Ni, Zn, Fe, Cu, Mg, alkali metal, or combinations thereof;

- 5 -

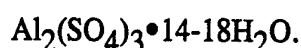
C = HSO₄, SO₄, NO₃, PO₄, HPO₄, BF₄, H₂PO₄ or combinations thereof;

n = an integer from 1 to 5;

m = 5 - n; and

5 h = an integer ranging from 0 to 20.

Examples of preferred water soluble fillers within formula II include those wherein C is SO₄, with the most preferred water soluble filler being



Particularly preferred erodable filler agglomerates of the invention are those
10 wherein the agglomerating agent consists essentially of the water soluble filler Al₂(SO₄)₃•14-18H₂O and the water insoluble filler consists essentially of Na₃AlF₆ (cryolite).

The erodable filler agglomerates of the invention are formed in situ (i.e., a "one step method") in the coatable mixture of the present invention. The
15 erodable filler agglomerates formed in situ are ideally suited for use as active fillers in abrasive articles. Alternatively, the erodable filler agglomerates may be separated from a first coatable mixture and used in a second coatable mixture which may be the same or different from the first coatable mixture (i.e., a "two step method").

20 Suitable binders for the abrasive articles of this invention comprise a cured organic resin, the organic resin selected from the group consisting of phenolic resins, aminoplast resins, urethane resins, epoxy resins, acrylic-based resins, acrylated isocyanurate resins, urea-aldehyde resins, isocyanurate resins, acrylated urethane resins, acrylated epoxy resins, and mixtures thereof.

25 In the case of a coated abrasive article, one preferred coated abrasive article has a size coating comprising the erodable filler agglomerates described above, and a make coating. A preferred make coating comprises an organic resin and titanium dioxide. The addition of titanium dioxide, particularly to phenolic resins, improves the cured binder properties, increasing both the wet and dry hardness.
30 Titanium dioxide also increases the surface tension of the uncured make coating, which tends to orient the abrasive grains with a sharp point distal from the

- 6 -

backing. Unexpectedly, the combination of the erodable filler agglomerates in the size coating, with titanium dioxide in the make coating, appears to have a synergistic effect to increase the abrading performance of coated abrasives.

Another preferred coated abrasive in accordance with the present invention
5 comprises a plurality of erodable filler agglomerates, as above described, and a plurality of abrasive particles, both the erodable filler agglomerates and the abrasive particles dispersed throughout and adhered within a binder attached to a substrate or backing. The abrasive articles of this embodiment are made using slurry of the erodable filler agglomerates and abrasive particles in a binder
10 precursor which is coatable or capable of being rendered coatable. The slurry is coated or spread onto a backing and the coated backing subsequently subjected to conditions which cure the binder precursor. In bonded abrasives, the mixture is placed in a mold and subjected to conditions which cure the binder precursor. Heat and/or radiation energy are suitable conditions under which the binder
15 precursor herein may be cured.

A method of preparing a coatable mixture containing erodable filler agglomerates and binder precursor, as above described, is another aspect of the invention, the method including the steps of:

- 20 (a) mixing water soluble filler with a sufficient amount of water and at a temperature sufficient to dissolve at least a portion of the water soluble filler to form a solution comprising the water soluble filler;
- (b) separately combining water insoluble filler, binder precursor, and water in proportions and at a temperature sufficient to form a dispersion comprising the water insoluble filler;
- 25 (c) combining the solution of step (a) with the dispersion of step (b) to form a coatable mixture from which erodable filler agglomerates will form in situ in the coatable mixture; and
- (d) allowing the formation of erodable filler agglomerates comprising a plurality of individual particles of water insoluble filler
30 agglomerated in the coatable mixture in situ by an agglomerating agent, the agglomerating agent being as above described.

- 7 -

The immediately-above described method is a preferred "one-step" method of producing the coatable mixture of the invention. Optionally, a "two step" procedure may be employed wherein after step (d), the coatable mixture is diluted with organic solvent to render the mixture filterable (step e), the diluted mixture
5 passed through a filtering means, such as filter paper, wire screen, and the like, to separate the erodable filler agglomerates from the liquid portion (step f), and the erodable filler agglomerates added to a second coatable mixture being the same as or different from the coatable mixture of either of steps (c) or (d), or both. Thus, the erodable filler agglomerates themselves are an aspect of the invention,
10 having composition as above described.

Methods of making coated abrasive articles are also presented, one of the methods including the steps of coating one side of a backing with a make coating, applying to the make coating a plurality of abrasive particles, subjecting the make coating to conditions which partially cure the make coating, coating the resulting
15 structure with one of the coatable mixtures prepared by the processes described immediately above to form a size coating, and subjecting the make and size coatings to conditions which cure the make and size coatings. Another method comprises combining abrasive particles with the coatable mixture produced in step (c) above to form a coatable abrasive slurry, coating one side of a backing with
20 the coatable abrasive slurry, and subjecting the coated backing to conditions which cure the binder precursor.

FIG. 1 shows a scanning electron micrograph (SEM, 200x magnification) of prior art cryolite particles;

FIG. 2 shows an SEM (200x magnification) of one erodable filler
25 agglomerate made in accordance with the method of the invention; and

FIG. 3 shows an SEM (50x magnification) of a plurality of erodable filler agglomerates made in accordance with the method of the invention.

It has been observed that during the preparation of certain coatable mixtures, the presence of certain water soluble fillers causes certain water
30 insoluble filler particles to agglomerate in situ. Although not wishing to be bound by any theory, it may be possible that in the presence of the water insoluble filler

- 8 -

the water soluble filler experiences a common ion effect, wherein the presence of an insoluble or slightly water soluble salt decreases the solubility of a normally very soluble or infinitely water soluble filler having an ion in common with the insoluble or slightly soluble salt. Surprisingly, it has been observed that when the

5 coatable mixtures of the invention were prepared with calcium carbonate or potassium tetrafluoroborate as water insoluble fillers, the presence of aluminum sulfate did not cause either the calcium carbonate or potassium tetrafluoroborate particles to agglomerate.

A preferred coatable mixture of the invention will comprise (on a dry

10 weight basis) between 30 to 60 weight percent binder; preferably between 30 to 60 weight percent cryolite, and less than 10 weight percent, more preferably 5 weight percent, even more preferably 2 weight percent aluminum sulfate $[\text{Al}_2(\text{SO}_4)_3 \cdot 14-18\text{H}_2\text{O}]$. At levels even as low as 0.5 weight percent or lower, the presence of $\text{Al}_2(\text{SO}_4)_3 \cdot 14-18\text{H}_2\text{O}$ water soluble filler has had a positive effect

15 on the abrading performance of coated abrasives made using coatable mixtures of the invention. The water soluble filler $\text{Al}_2(\text{SO}_4)_3 \cdot 14-18\text{H}_2\text{O}$ is commonly referred to in the inorganic chemical art as "aluminum sulfate 16", the "16" referring to the average degree of hydration of $\text{Al}_2(\text{SO}_4)_3 \cdot 14-18\text{H}_2\text{O}$. Water soluble fillers useful in the invention, such as $\text{Al}_2(\text{SO}_4)_3 \cdot 14-18\text{H}_2\text{O}$, and water

20 insoluble fillers, such as cryolite, are available from various inorganic chemical suppliers.

Particularly preferred inorganic halide salts suitable for use in the coatable mixtures of the present invention include cryolite (Na_3AlF_6) and "cryolite derivatives" such as $\text{Li}_3\text{Na}_3(\text{AlF}_6)_2$, $(\text{NH}_4)_2\text{GaF}_6$ and the like. The invention

25 also contemplates using mixtures of these as the water insoluble filler. Particularly preferred is the inorganic halide salt cryolite.

In addition to the above mentioned components, the coatable mixture comprises water sufficient to dissolve the water soluble filler and optional organic solvent to lower the coatable mixture viscosity so that it is easier to process.

30 Typically, and preferably, during curing of the binder precursor, water and optional organic solvent are removed. (Alternatively, a reactive diluent may be

SUBSTITUTE SHEET

- 9 -

employed which reacts with the binder precursor and remains in the cured binder.) Since aluminum sulfate and other water soluble fillers may be insoluble in alcohol solvents such as ethylene glycol monobutyl ether, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, and the like, the use of these or other
5 solvents which tend to increase the viscosity of the coatable mixture of the invention should be held to a minimum. It is preferred that the coatable mixture contain at least 0.5 weight percent of one of the above-mentioned solvents per total weight of coatable mixture for viscosity reduction; however, if more than 50
10 weight percent of one of these solvents, based on total coatable mixture weight, is used the water soluble filler may precipitate out of the coatable mixture, which may inhibit formation of the erodable filler agglomerates.

In the preparation of coatable mixtures containing erodable filler agglomerates, it is preferred that the water soluble filler be at least partially dissolved in water in a first container to form a solution. More preferably, the
15 water soluble filler is completely dissolved in water to form an unsaturated or saturated solution of the water soluble filler. Supersaturated solutions of the water soluble filler are not preferred as they appear to achieve no additional benefit, although they are not without the scope of the invention. In a second container, binder precursor, water, water insoluble filler particles, and any optional additives
20 and optional organic solvent are mixed together to form a dispersion of water insoluble filler particles. Subsequently, the solution of water soluble filler is combined with the dispersion of the second container. The water soluble filler may alternatively be added directly to the binder precursor. However, it has been found easier to consistently prepare a uniform coatable mixture if the water soluble
25 filler is first at least partially dissolved in water. Either one or both of the solution and dispersion may be heated slightly to speed dissolving of the water soluble filler or dispersion of the water insoluble filler, or to render the resulting coatable mixture slightly less viscous, but this has not been found to be necessary or even desired.

30

- 10 -

One specifically preferred coatable mixture of the invention comprises an 82 percent by weight solids solution used to form a size coating which comprises (weight basis)

5	76% (wt) solids phenolic resin	51.80 parts
	cryolite	41.75
	41.7% aqueous $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{-}18\text{H}_2\text{O}$ solution	2.04
	water	3.85
	ethylene glycol monoethyl ether	0.56
		(100.00).

10

The phenolic resin, water and ethylene glycol monoethyl ether are blended and then heated to 40°C. (It is not necessary to heat the solution to form the erodable filler agglomerates of the invention, but heating renders the solution easier to further process.) Cryolite is added to the solution and the solution agitated to form
 15 a dispersion of the cryolite in the liquid components. The aqueous $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{-}18\text{H}_2\text{O}$ is then added slowly to the cryolite dispersion and the erodable filler agglomerates form in situ and may be detected visually without the use of magnification.

The coatable mixture may then be applied as a size coating over abrasive
 20 particles and a make coating, or abrasive particles may be added to the coatable mixture to form a coatable abrasive slurry. The abrasive slurry is then coated or spread onto a backing in the course of manufacturing an abrasive article. In a preferred coating operation it has been found desirable to heat the coatable mixture to a temperature ranging from 40°C to 50°C in order to reduce the coatable
 25 mixture viscosity slightly.

As stated in the Summary of Invention, "water soluble" and "water insoluble" are meant to reflect the approximate water solubility of the filler components in "cold water" (0 - 50°C). Table A presents a compilation of published water solubilities of some fillers within formulas I and II, compiled from
 30 The Handbook of Chemistry and Physics, 58th Ed., CRC Press, Inc., West Palm Beach, Florida, pp. B-85 et. seq. The terms "slightly soluble", "soluble" and "very soluble" are defined according to the United States Pharmacopeia in Table B, which is Table 85 of Grant & Hackh's Chemical Dictionary, 5th Ed., McGraw-Hill (1987) page 541.

- 11 -

It can be seen from Table A that the water soluble filler and water insoluble filler must be chosen with the relative solubilities of the species in mind. For example, one would not expect as much success in agglomerating cryolite with ZnSO_4 , as one would expect success agglomerating cryolite with $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$.

- 5 However, to optimize grinding efficiency, depending on the grinding conditions, workpiece, etc., the solubility of the water soluble filler will be selected accordingly.

Preferably, the water insoluble fillers are selected from inorganic halide salts within formula I above; most preferably the water insoluble filler is cryolite.

- 10 Within formula II above, "B" of the water soluble filler is preferably selected from the group consisting of: alkali metal, aluminum, ammonium, nickel, zinc, iron, copper, magnesium, and combinations thereof. Particularly preferred as "B" are aluminum, nickel and zinc, with aluminum being most preferred. The most preferred "C" is SO_4 ; however, it is within the scope of this invention to
15 utilize a combination of water soluble fillers in the erodable filler agglomerates. The value of h is also significant in that the preferred degree of hydration (i.e., "h") is dependent upon "B" and "C".

20

25

30

- 12 -

Table A: Filler Solubilities

<u>Fillers</u>		<u>Sol. in cold* H₂O.</u>
<u>Water Soluble Fillers</u>		<u>parts filler/100 parts H₂O</u>
5	Al ₂ (SO ₄) ₃	31.3 ⁰
	Al ₂ (SO ₄) ₃ •18H ₂ O	86.9 ⁰
	Al(NO ₃) ₃ •9H ₂ O	63.7 ²⁵
	CuSO ₄ •5H ₂ O	31.6 ⁰
	FeSO ₄ •5H ₂ O	soluble
10	FeSO ₄ •7H ₂ O	15.65
	Li ₂ SO ₄	26.1 ⁰
	Li ₂ SO ₄ •H ₂ O	34.9 ²⁵
	MgSO ₄	26 ⁰
	MgSO ₄ •7H ₂ O	71 ²⁰
15	(NH ₄) ₃ PO ₄ •3H ₂ O	26.1 ²⁵
	(NH ₄) ₂ HPO ₄	57.5 ¹⁰
	NH ₄ BF ₄	25 ¹⁶
	(NH ₄) ₂ SO ₄	70.6 ⁰
	NH ₄ HSO ₄	100
20	NaBF ₄	108 ²⁶
	Ni(NO ₃) ₂ •6H ₂ O	238.5 ⁰
	NiSO ₄	29.3 ⁰
	NiSO ₄ •6H ₂ O	62.52 ⁰
	NiSO ₄ •7H ₂ O	75.6 ^{15.5}
25	Na ₂ SO ₄	soluble
	Na ₂ SO ₄ •7H ₂ O	19.5 ⁰
	Na ₂ SO ₄ •10H ₂ O	11 ⁰
	Zn(NO ₃) ₂ •5H ₂ O	very soluble
	ZnSO ₄	soluble
30	ZnSO ₄ •7H ₂ O	96.5 ²⁰
	KH ₂ PO ₄	33 ²⁵
	Na ₂ HPO ₄ •2H ₂ O	100 ⁵⁰
<u>Water Insoluble Fillers</u>		
35	Na ₃ AlF ₆ (cryolite)	slightly soluble
	Li ₃ Na ₃ (AlF ₆) ₂	0.074 ¹⁸
	(NH ₄) ₂ GaF ₆	insoluble

* superscript indicates temperature, °C, where given

Table B: USP Solubility Classification

<u>Description</u>	<u>Parts of solvent required for 1 part solute</u>
5 Very soluble	less than 1
Freely soluble	1-10
Soluble	10-30
Sparingly soluble	30-100
Slightly soluble	100-1000
10 Very slightly soluble	1,000-10,000
Practically insoluble or insoluble	10,000+

A typical and preferred resole phenolic binder precursor solution has pH ranging from 8 to 10. The pH of the coatable mixtures of the invention may vary over a wide range, from 3.0 to 10, based on selection of binder precursor, water soluble filler type and amount, and other variables. It will be appreciated by those skilled in the coating art that the particularly preferred pH of the coatable mixtures within the invention will depend primarily on the binder precursor chosen, and secondarily on the water soluble filler, the ratio of ingredients, temperature and the like. Coatable mixture pH outside the range normally recommended for the particular binder precursor solution may have an adverse affect on binder precursor curing and or viscosity.

The water soluble filler is preferably no more than 10 weight percent (more preferably no more than 5 weight percent) of the total weight of water soluble and water insoluble fillers, but at least 10 weight percent (more preferably at least 50 weight percent) of the total weight of the agglomerating agent.

FIG. 1 shows a scanning electron micrograph (SEM, 200x magnification) of cryolite in its non-agglomerated form, whereas FIG. 2 shows an SEM (with identical magnification as FIG. 1) of an erodable filler agglomerate of the invention. The erodable filler agglomerate of FIG. 2 was formed using one preferred method of the invention, wherein 2.6 parts by weight (dry weight basis) of aluminum sulfate was substituted for a portion of the cryolite in the coatable mixture.

The erodable filler agglomerates of the present invention can vary widely in shape, size, surface contour, and the like, as evidenced by viewing the SEMs

- 14 -

of FIGs. 2 and 3 (the former at 200x magnification, the latter at 50x magnification). The largest dimension can range from 10 to 1000 micrometers, the average diameter not appearing to be critical. Typical useful average diameters fall within the range of from 10 to 100 micrometers. The erodable filler
5 agglomerates of the invention are not required to be any particular shape, with spheres, rods, pellets, and other conventional shapes being acceptable. Spherical erodable agglomerates may be preferred in situations where the erodable agglomerates of the invention are used in "thick" coatings, whereas pellet-shaped erodable filler agglomerates may be preferred for other coating geometries.

10 The erodable filler agglomerates of the invention may, of course, be screened to obtain a desired size or size distribution of erodable filler agglomerates. Thus, the range of sizes of the agglomerates of the invention can be controlled to a certain degree by the process conditions, ingredient ratios, etc. of the coatable mixture of the invention, and further by mechanical techniques
15 after the erodable filler agglomerates have been separated from their "mother" coatable mixture.

Consideration of the abrasive particle size used in the abrasive articles of the invention is also important in selecting erodable filler agglomerate size and size distribution. The ratio of the average diameter of the abrasive particles to the
20 average diameter of the erodable filler agglomerates of the invention may range from 2.5:1 to 0.5:1.

The erodability characteristics of the erodable filler agglomerates of the invention, i.e. the rate of breakdown or erosion under a given set of chemical and/or mechanical forces, can be varied by varying the water soluble and insoluble
25 filler identity, relative amounts, or both. For example, erodable filler agglomerates of the invention having a greater percentage of water soluble filler component will erode more quickly and present fresh water insoluble filler particles to the workpiece faster than agglomerates having a lower percentage of water soluble filler.

30 As mentioned in the Summary of the Invention, it is possible to separate the erodable filler agglomerates of the invention from the coatable mixture form

- 15 -

which they were formed, typically and preferably by reducing the viscosity of the coatable mixture to render it filterable or screenable. Organic solvents, such as aliphatic alcohols, may be used for viscosity reduction, as well as ethers.

Once separated from their "mother" coatable mixture, the erodable filler
5 agglomerates of the invention appear to be stable indefinitely. Preferably, the erodable filler agglomerates of the invention are kept in a closed container, at room temperature (25 °C), to avoid extremes of humidity and temperature, obviously to ensure that the agglomerates do not absorb a substantial amount of water to the extent that the erodable agglomerates degrade to essentially non-
10 agglomerated filler, or lose water of hydration. Of course, the container and erodable filler agglomerates are preferably not allowed to experience extremes of mechanical forces, which might cause the erodable filler agglomerates of the invention to mechanically degrade prematurely.

The separated erodable filler agglomerates may then be used in a "two-
15 step" process wherein a second coatable mixture is formed, and the previously formed erodable filler agglomerates added thereto. Of course, preformed erodable filler agglomerates may be added to a coatable solution in which another set of erodable filler agglomerates is to be formed, which may be the same or different than the preformed erodable filler agglomerates.

20 The coatable mixture may comprise materials other than binder precursor and erodable filler agglomerates. Materials commonly utilized in abrasive articles as additives include non-agglomerated fillers, coupling agents, wetting agents, dyes, pigments, plasticizers, release agents and combinations thereof. Non-agglomerated fillers, such as grinding aids, encompass a wide variety of different
25 materials and can be inorganic or organic based. Examples of suitable grinding aids for use in the present invention include waxes, organic halide compounds, non-aluminum containing halide salts, and metals and their alloys. Examples of organic halide compounds include chlorinated waxes, tetrachloronaphthalene, pentachloronaphthalene, and polyvinyl chloride. Examples of non-aluminum based
30 halide salts include sodium chloride, potassium tetrafluoroborate, sodium tetrafluoroborate, silicon fluorides, potassium chloride, and magnesium chloride.

- 16 -

Examples of metals include tin, lead, bismuth, cobalt, antimony, cadmium, iron or titanium and mixtures thereof, all in their elemental forms. Other miscellaneous grinding aids include calcium carbonate, elemental sulfur, organic sulfur compounds, graphite and metallic sulfides. Examples of preferred non-
5 agglomerated fillers include calcium carbonate, calcium oxide, calcium metasilicate, titanium dioxide, alumina trihydrate, silica, kaolin, quartz and glass. The use of titanium dioxide in the make coating at a weight percentage ranging from 5 to 20 (dry weight basis) is preferred.

The amount of non-agglomerated filler or grinding aid will be typical of
10 that used in the particular type of abrasive article, with generally lower amounts of non-agglomerated fillers and grinding aids being employed when higher amounts of the erodable filler agglomerates formed in the coatable mixtures of the invention are employed.

Abrasive articles of the invention can be coated abrasives, nonwoven
15 abrasives or bonded abrasives.

Coated abrasive articles generally include a flexible backing selected from paper sheet, cloth fabric, film, vulcanized fiber, and the like. Cloth is preferred in wet grinding operations, and is preferably treated with an optional back side coating and an optional front side coating. There may be no clear line of
20 demarcation between the optional front and back side coatings, which may meet in the interior of the cloth backing, which is saturated as much as possible with the resins of those coating. Overlaying the optional front side coating, if used, may be a make coating in which are embedded abrasive particles. A size coating containing the erodable filler agglomerates may then be coated over the make
25 coating and the abrasive particles.

In some instances coated abrasives comprise a supersize coating overlaying the size coating, and coated abrasives of this invention are no different in this respect.

In coated abrasives of the present invention, at least one of the coatings
30 described above includes the erodable filler agglomerates of the invention. It is preferred that the erodable filler agglomerates of the invention be present in the

- 17 -

outermost layer of coated abrasives of the invention, i.e, the size or supersize coating.

Alternatively, rather than using make and size coatings, a slurry comprising abrasive particles, erodable filler agglomerates, binder precursor, water, and
5 optional non-agglomerated additives and optional organic solvent, may be coated onto a backing. This coating (upon curing of the binder precursor) then serves as the abrasive layer.

Nonwoven abrasive products typically include an open, porous, lofty, filamentous structure having abrasive particles distributed throughout the structure
10 and adherently bonded thereto by a binder. The nonwoven abrasives of the invention are preferably of like construction, substituting the binder made using the coatable mixtures of the invention described above. Bonded abrasives incorporating the above-described erodable filler agglomerates typically consist of a shaped mass of abrasive grains held together by a binder. The shaped mass can
15 be in any number of conventional forms such as wheels, points, discs, and cylinders, but is preferably in the form of a grinding wheel. A preferred bonded abrasive product in accordance with the present invention comprises between 50 to 90 weight percent abrasive grains dispersed and adhered within the binder. Bonded abrasives products are preferably manufactured by a molding process, and
20 are made with varying degrees of porosity to control the breakdown. The "coatable" mixture in these embodiments need only be "pourable" so that the mixture can be poured into a mold or onto a surface.

In the initial steps for making the abrasive articles of the invention, a coatable mixture of the invention comprising a binder precursor and erodable filler
25 agglomerates is applied to a backing in an uncured or unpolymerized state. Then, during further processing, the binder precursor is cured or polymerized to form a cured binder.

It is contemplated that radiation energy-curable resins may be used as the binder precursor of any of the coatings described above for coated abrasive articles
30 of the invention or for the binder in nonwoven and bonded abrasives. Examples

- 18 -

of radiation energy-curable resins are described in U.S. Pat. Nos. 4,715,138; 4,903,440, and 4,927,431.

Abrasive articles may also have release/and or load resistant coatings as supersize coatings, and may have pressure sensitive adhesive coatings on the back
5 side, as desired. Examples of suitable release coatings include crosslinked siloxanes formed from the condensation reaction product of hydrolyzed trialkoxysilane-terminated polydimethylsiloxanes. One suitable pressure sensitive adhesive for use in attaching abrasive articles to substrates is a 95.5:4.5 copolymer mixture of isooctylacrylate and acrylic acid.

10 The abrasive particles used in the abrasive articles of the invention may be individual abrasive grains or agglomerates of individual abrasive grains. Suitable abrasive particles for use in the present invention include those organic and inorganic particles having a Moh hardness greater than 7, more preferably from 9 to 10. If agglomerated, the abrasive particles may themselves be erodable, such
15 as disclosed in U.S. Pat. No. 4,652,275. The abrasive agglomerates, if used, will preferably range from 150 micrometers to 3000 micrometers in the largest dimension. If the individual abrasive grains are very fine, for example, corresponding to P 180 (FEPA-Norm), then between 10 and 1000 individual grains would be contained in each agglomerate. If the individual abrasive grains
20 correspond to P 36, then between 2 and 20 grains would be contained in each agglomerate. If agglomerated, the abrasive particles are typically irregular in shape, but they can also be formed into spheres, spheroids, ellipsoids, pellets, rods, or other conventional shapes. Combinations of individual abrasive grains can be used along with agglomerated abrasive grains, and the proportion of individual
25 abrasive grains employed in this manner may be as high as 70 percent of the weight of the abrasive agglomerates.

Examples of abrasive particles meeting the above and thus preferred in the practice of this invention include silicon carbide (including refractory silicon carbide such as disclosed in U.S. Pat. No. 4,505,720), aluminum oxide, alumina
30 zirconia (including fused alumina zirconia such as disclosed in U.S. Pat. Nos. 3,781,172; 3,891,408; and 3,893,826 commercially available from the Norton

- 19 -

Company of Worcester, Mass., under the trade designation "Norzon," cubic boron nitride, garnet, pumice, sand, emery, mica, corundum, quartz, diamond, boron carbide, fused alumina, sintered alumina, alpha alumina-based ceramic material (available from Minnesota Mining and Manufacturing Company, St. Paul, MN, 5 under the trade designation "Cubitron") as disclosed in U.S. Pat. Nos. 4,314,827; 4,518,397; 4,574,003; 4,770,671; 4,744,802; and 4,881,451 and combinations thereof. The preferred abrasive particles are aluminum oxide and silicon carbide.

The abrasive articles of the present invention may also include nonabrasive or less abrasive inorganic diluent grains as disclosed in U.S. Pat. No. 5,011,512, 10 i.e., nonabrasive inorganic diluent grains having a hardness less than 200 on the Knoop Hardness Scale. Useful nonabrasive diluent grain include limestone and gypsum.

The following non-limiting examples will further illustrate the invention. All formulation percentages and parts are based upon weight. The phenolic resole 15 resin used in each case was based on a 1.7:1 formaldehyde to phenol ratio, 76 weight percent solids resin. Where used, "aluminum sulfate" refers to $\text{Al}_2(\text{SO}_4)_3 \cdot 14-18\text{H}_2\text{O}$.

EXAMPLES

20 General Procedure For Making Coated Abrasives (I)

For the following examples made using this procedure, the backing of each coated abrasive consisted of a Y weight woven polyester cloth which had a four over one weave. Each backing was saturated with a latex/phenolic resin and then placed in an oven to partially cure this resin. Next, a calcium carbonate-filled 25 latex/phenolic resin pretreatment coating was applied to the back side of each backing. Each coated backing was heated to 120°C and maintained at this temperature until the resin had cured to a tack-free state. Finally, a pretreatment coating of latex/phenolic resin was applied to the front side of each coated backing and each coated backing was heated to 120°C and maintained at this temperature 30 until the resin had pre-cured to a tack-free state. Each backing made by this procedure was completely pretreated and was ready to receive a make coat.

- 20 -

A coatable mixture for making a make coating for each coated backing was prepared by mixing 69 parts of 70% solids phenolic resin (48 parts phenolic resin), 52 parts non-agglomerated calcium carbonate filler (dry weight basis), and enough of a solution of 90 parts water/10 parts ethylene glycol monoethyl ether to form
5 a make coating in each case which was 84% solids, with a final coating weight of 230 g/m^2 . The make coating was applied in each case via two-roll coating. (It will be appreciated that other coating methods, such as knife coating, curtain coating, spray coating, and the like, may have been used as well. Also, the number of rolls in roll coating is not required to be two.)

10 Next, grade 40 (ANSI standard B74.18 average particle size of 420 micrometers) heat-treated aluminum oxide abrasive particles were electrostatically coated onto the uncured make coatings with a weight of 760 g/m^2 .

Then the resulting constructions were heated for 15 minutes at 65°C to partially cure the make coating followed by further heating at 88°C for 75
15 minutes.

An 82% solids coatable mixture suitable for forming a size coating (having the compositions described in the following examples) was then applied to each coated abrasive via two-roll coating method over the abrasive particles/make coat construction. The resulting coated abrasives received a thermal cure of 90 minutes
20 at 88°C followed by 12 hours at 100°C .

After this thermal cure, the coated abrasives were single flexed (i.e. passed over a roller at an angle of 90° to allow a controlled cracking of the make and size coatings).

25 General Procedure for Making Coated Abrasives (II)

The following examples that did not use General Procedure for Making Coated Abrasives (I) used the following procedure. The pretreated backing of each of the coated abrasives made according to the General Procedure for Making Coated Abrasives (II) was the same as the pretreated backing described above
30 under the heading General Procedure for Making Coated Abrasives (I).

- 21 -

A coatable mixture suitable for producing a make coat for each coated backing was prepared by mixing 69 parts of 70% solids phenolic resin (48 parts phenolic resin), 13.5 parts titanium dioxide filler, 38.5 parts calcium carbonate filler, and enough of a solution of 90 parts water/10 parts ethylene glycol monoethyl ether to form a make coating which was 84% solids which was coated
5 via a two-roll coater to achieve a cured coating weight of about 140 g/m^2 .

Next, grade 40 (ANSI standard B74.18 average particle size of 420 micrometers) heat treated aluminum oxide abrasive particles were electrostatically coated onto the uncured make coating with a weight of 760 g/m^2 .
10 Then the resulting constructions received a precure of 15 minutes at 65°C , followed by 75 minutes at 88°C . A 82% solids coatable mixture suitable for forming a size coating (having the compositions described in the following examples) was then applied over the abrasive particles/make coat construction via two-roll coater. The size coating weight in each case was 280 g/m^2 . The
15 resulting coated abrasives received a thermal cure of 30 minutes at 88°C followed by 12 hours at 100°C . After this thermal cure, the coated abrasives were flexed as in General Procedure for Making the Coated Abrasive I.

Test Procedure I (Wet Grinding)

20 The coated abrasive material was attached to the periphery of a 36 cm diameter metal wheel. The effective cutting area of the abrasive segment was 2.54 cm by 109 cm. The workpiece abraded by these segments was 1018 steel, 1.27 cm width by 36 cm length by 7.6 cm height. Abrading was conducted along the 1.27 cm by 36 cm face. The workpiece was mounted on a reciprocating table,
25 while the metal wheel speed was 1500 rpm or 1674 surface meters per minute. The table speed at which the workpiece traversed was 9 meters/minute. The down feed increment of the wheel was 45 micrometers/pass of the workpiece. This abrading process emulated conventional wet surface grinding wherein the workpiece was reciprocated beneath the rotating contact wheel with incremental
30 down feeding between each pass. The grinding was carried out under a water flood, and the test endpoint was when the normal force exceeded 12.6 kg/cm^2 .

- 22 -

The amount of workpiece removed by each coated abrasive example was measured and recorded in grams.

Test Procedure II (Dry Grinding)

5 The coated abrasive was converted into a 7.6 cm by 335 cm endless belt and installed on a constant load surface grinder. A preweighed, 304 stainless steel workpiece (approximately 2.5 cm by 5 cm by 18 cm) was mounted in a holder and was positioned vertically with the 2.5 cm by 18 cm face confronting an
10 wheel with one to one land to groove ratio, over which was entrained the coated abrasive belt. The workpiece was then reciprocated vertically through a 18 cm path at the rate of 20 cycles per minute, while a spring loaded plunger forced the workpiece against the belt with a load of 11 kg as the belt was driven at 2050 meters per minute. After one minute of elapsed grinding time, the workpiece
15 holder assembly was removed and reweighed. The amount of workpiece removed was calculated by subtracting the weight of the workpiece after abrasion from its original weight. Then a new, preweighed workpiece and holder were mounted on the equipment. The test endpoint was 5 minutes. The experimental error on this test was +/- 10%.

20

Test Procedure III (Dry Grinding)

The test method of Test Procedure III was essentially the same as Test Procedure II except that the workpiece being abraded was 4150 steel, and the test endpoint was when the amount of 4150 steel removed was less than 40 grams in
25 a one minute interval.

Test Procedure IV (Wet Grinding)

The test method of Test Procedure IV was essentially the same as Test Procedure I except for the following changes. The table speed at which the
30 workpiece traversed was 12 meters/minute. The down feed increment of the wheel

- 23 -

was 40 micrometers/pass of the workpiece. The test endpoint was when the normal force exceeded 14 kg/cm^2 .

Test Procedure V (Dry Grinding)

- 5 The test method of Test Procedure V was essentially the same as Test Procedure I except for the following changes. The table speed at which the workpiece traversed was 18 meters/minute. The down feed increment of the wheel was 50 micrometers/pass of the workpiece. The grinding was done dry, i.e., there was no water flood. The test endpoint was when the coated abrasive began to
- 10 shell, i.e., the premature release of the abrasive grains.

Test Procedure VI (Wet Grinding)

- The test method of Test Procedure VI was essentially the same as Test Procedure IV except for the following changes. The table speed at which the
- 15 workpiece traversed was 18 meters/minute. The test endpoint was either shelling or when the normal force exceeded 14 kg/cm^2 .

Test Procedure VII (Wet Grinding)

- The test method of Test Procedure VII was essentially the same as Test
- 20 Procedure I except for the following changes. The table speed at which the workpiece traversed was 12 meters/minute. The down feed increment of the wheel was 50 micrometers/pass of the workpiece. The test endpoint was when the normal force exceeded 11.8 kg/cm^2 .

25 Control Examples A & B, Example 1

- The coated abrasives for this set of Examples were made according to the General Procedure for Making Coated Abrasives (I). The size coating in each case was prepared by mixing, in addition to resin and filler, enough of a 90 parts water/10 parts ethylene glycol monoethyl ether solution to make an 82% solids
- 30 size coat, with a final coating weight of 300 g/m^2 . The size coating for Control Example A included 69 parts of 70% solids phenolic resin (48 parts phenolic

- 24 -

resin), and 52 parts calcium carbonate filler. The size coating for Control Example B included 52 parts cryolite and 69 parts of 70% solids resole phenolic resin (48% phenolic resin). The size coating for Example 1 included 49.4 parts cryolite, agglomerated by the addition of 2.6 parts aluminum sulfate, and 48 parts resole phenolic resin, each on a dry weight basis. For Example 1 the aluminum sulfate was added directly to the phenolic resin as a solid. These coated abrasives were tested under Test Procedure I and Test Procedure II. The results can be found in Tables 1 and 2 respectively.

10 Table 1 (Test Procedure I, Wet Grinding)

<u>Example</u>	<u>Workpiece removed (gms)</u>
Control A	700
Control B	696
1	1315

15

Table 2 (Test Procedure II, Dry Grinding)

<u>Example</u>	<u>Workpiece removed (gms)</u>
Control A	111
Control B	124
1	141

20

Control Examples A & C, Examples 2 to 6

The coated abrasives for this set of Examples were made according to the General Procedure for Making Coated Abrasives (I). The size coating for Control Example A was the same as described above.

The size coating for Control Example C included 52 parts cryolite and 48 parts resole phenolic resin, each on a dry weight basis and the size coating weight was 330 g/m².

The size coating for Example 2 included 49.4 parts cryolite, agglomerated by the addition of 2.6 parts aluminum sulfate and 48 parts resole phenolic resin, all on a dry weight basis, and the size coating weight was 306 g/m².

- 25 -

The size coating for Example 3 consisted of 49.9 parts cryolite, agglomerated by the addition of 2.1 parts aluminum sulfate, and 48 parts resole phenolic resin, all on dry weight basis, and the size coating weight was 306 g/m².

The size coating for Example 4 consisted of 50.4 parts cryolite, 5 agglomerated by the addition of 1.6 part aluminum sulfate and 48 parts resole phenolic resin (dry weight basis), and the size coat weight was 293 g/m².

The size coating for Example 5 consisted of 51 parts cryolite, agglomerated with 1.0 part aluminum sulfate, and 48 parts resole phenolic resin, and the size coating weight was 311 g/m².

10 The size coating for Example 6 consisted of 51.5 parts cryolite, agglomerated with 0.5 part aluminum sulfate, and 48 parts resole phenolic resin, and the size coating weight was 297 g/m².

For Examples 2-6 the aluminum sulfate was added directly to the phenolic resin as a solid. In each size coating, enough of a 90/10 water/ethylene glycol 15 monoethyl ether solution was added to form an 82% solids solution. These coated abrasives were tested under Test Procedure I and Test Procedure II. The results can be found in Tables 3 and 4 respectively.

Additionally, the coated abrasives made according to Control Example C and Example 2 were tested under the Test Procedure III and the results can be 20 found in Table 5.

Table 3 (Test Procedure I, Wet Grinding)

	<u>Example</u>	<u>Workpiece removed (gms)</u>
	Control A	751
25	Control C	816
	2	1103
	3	1125
	4	1031
	5	1075
30	6	784

- 26 -

Table 4 (Test Procedure II, Dry Grinding)

5	<u>Example</u>	<u>Workpiece removed (gms)</u>
	Control A	119
	2	142
	3	134
	4	129
	5	128
	6	124

10

Table 5 (Test Procedure III, Dry Grinding)

15	<u>Example</u>	<u>Workpiece removed (gms)</u>
	Control C	1754
	2	1864

15

Control Examples D & E; Examples 7 through 9

The coated abrasives for this set of examples were tested according to Test Procedures IV, V, VI and VII. The abrading results can be found in Tables 6, 7, 8 and 9 respectively.

20 Control Example D coated abrasive was a grade 40 Resin Bond Cloth Type ZB coated abrasive known under the trade name "Three-M-ite" commercially available from the Minnesota Mining and Manufacturing Company, St. Paul, MN. This particular coated abrasive contained calcium carbonate in the size coating and did not contain cryolite in the size coating.

25 The coated abrasives for Control Example E and Examples 7 through 9 were made according to the General Procedure For Making Coated Abrasives (I) except that the make coating weight was 140 g/m^2 .

The size coating weight for Control E and Examples 7 through 9 was 275 g/m^2 .

30 The size coating for Control Example E consisted of 52 parts cryolite and 48 parts resole phenolic resin (dry weight basis).

- 27 -

The size coating for Example 7 consisted of 51.5 parts cryolite, 0.5 part aluminum sulfate and 48 parts resole phenolic resin (dry weight basis).

The size coating for Example 8 consisted of 51.0 parts cryolite, 1.0 part aluminum sulfate and 48 parts resole phenolic resin (dry weight basis).

5 The size coating for Example 9 consisted of 50.4 parts cryolite, 1.6 part aluminum sulfate and 48 parts resole phenolic resin (dry weight basis).

For Examples 7 through 9, the aluminum sulfate was added to the cryolite/phenolic resin/solvent suspension as a 41.7% aqueous solution, and enough of a 90/10 water/ethylene glycol monoethyl ether solution was added to
10 form an 82% solids size coating solution.

Coated abrasives D, E, and 7-9 were tested in accordance with Test Procedures IV - VII, with the results presented in Tables 6-9, respectively.

Table 6 (Test Procedure IV, Wet Grinding)

15	<u>Example</u>	<u>Workpiece removed (gms)</u>
	Control D	701
	Control E	666
	7	1198
	8	1272
20	9	1194

Table 7 (Test Procedure V, Dry Grinding)

	<u>Example</u>	<u>Workpiece removed (gms)</u>
	Control D	848
25	Control E	873
	7	1521
	8	1395
	9	1511

30

- 28 -

Table 8 (Test Procedure VI, Wet Grinding)

	<u>Example</u>	<u>Workpiece removed (gms)</u>
	Control D	404
	Control E	435
5	7	693
	8	653
	9	559

10 **Table 9 (Test Procedure VII, Wet Grinding)**

	<u>Example</u>	<u>Workpiece removed (gms)</u>
	Control D	668
	Control E	674
	7	1058
15	8	1045
	9	1036

Control Examples D & F; Examples 10 through 12

20 The coated abrasives for Control Example F and Examples 10 through 12 were made according to the General Procedure for Making Coated Abrasives (II). The size coating for Control Example E included 52 parts cryolite and 48 parts resole phenolic resin; the size coating for Example 10 included 51.5 parts cryolite, 0.5 part aluminum sulfate and 48 parts resole phenolic resin; the size coating for

25 Example 11 included 51.0 parts cryolite, 1.0 part aluminum sulfate and 48 parts resole phenolic resin; and the size coating for Example 12 consisted of 50.4 parts cryolite, 1.6 part aluminum sulfate and 48 parts resole phenolic resin (dry weight basis in each case). For Examples 10 through 12, the aluminum sulfate was added

30 enough of a 90/10 water/ethylene glycol monoethyl ether solution was added in each case to form an 82% solids size coating solution.

- 29 -

The coated abrasives for this set of examples were tested according to Test Procedure IV, V, VI and VII. The abrading results can be found in Tables 10, 11, 12 and 13 respectively.

5

Table 10 (Test Procedure IV, Wet Grinding)

<u>Example</u>	<u>Workpiece removed (gms)</u>
Control D	701
Control F	742
10	1663
11	1590
12	1355

10

Table 11 (Test Procedure V, Dry Grinding)

<u>Example</u>	<u>Workpiece removed (gms)</u>
Control D	848
Control F	969
10	1548
11	1697
12	1251

15

20

Table 12 (Test Procedure VI, Wet Grinding)

<u>Example</u>	<u>Workpiece removed (gms)</u>
Control D	404
Control F	457
10	713
11	774
12	665

25

30

- 30 -

Table 13 (Test Procedure VII, Wet Grinding)

	<u>Example</u>	<u>Workpiece removed (gms)</u>
	Control D	668
	Control F	627
5	10	1135
	11	1165
	12	1042

Control Examples B and D and Examples 13 through 37

- 10 This set of examples compared the performance of coated abrasives which contained various sulfate salts as water soluble filler in the size coating. The coated abrasives were made according to the General Procedure for Making Coated Abrasives (I), except that the make coating weight was 170 g/m^2 in each case. The size coating contained 48 parts resole phenolic resin and 52 parts sulfate salt/cryolite in each case (dry weight basis). The weight percentages of the sulfate salt and cryolite, along with the size coating weight can be found in Table 14.

For Examples 13 through 18 the sulfate salt was sodium sulfate (Na_2SO_4).

For Examples 19 through 22 the sulfate salt was aluminum sulfate $[\text{Al}_2(\text{SO}_4)_3 \cdot 14-18\text{H}_2\text{O}]$.

- 20 For Example 23 the sulfate salt was ammonium sulfate $[\text{NH}_4)_2\text{SO}_4]$.
 For Example 24 the sulfate salt was ammonium bisulfate (NH_4HSO_4).
 For Examples 25 and 26 the sulfate salt was nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$).
 For Examples 27 and 28 the sulfate salt was zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$).
 For Examples 29 and 30 the sulfate salt was iron sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$).
 25 For Examples 31 and 32 the sulfate salt was copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$).
 For Examples 33 and 34 the sulfate salt was magnesium sulfate (MgSO_4).
 For Examples 35 through 37 the sulfate salt was lithium sulfate ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$).
 30 In each Example B, D, 13-29 and 23-37, the solvent used was a 90/10 water/ethylene glycol monoethyl ether solution; in Examples 21 and 22, a 90/10

- 31 -

parts solution of water/propylene glycol monomethyl ether was employed to form an 82% solids size coating solution. The coated abrasives were tested according to Test Procedure VI (Wet Grinding) and the results can be found in Table 14.

5

Table 14

<u>Example</u>		<u>% sulfate salt/ % cryolite</u>	<u>size coat weight (gms/m²)</u>	<u>workpiece removed (gms)</u>
Control B		0/52	420	471
Control D		0/52	220*	495
10	13	0.5/51.5	402	457
	14	1.0/51.0	430	534
	15	1.6/50.4	390	672
	16	2.1/49.9	410	506
	17	2.6/49.4	400	567
15	18	3.2/48.8	385	623
	19	0.5/51.5	410	495
	20	1.0/51.0	410	517
	21	0.5/51.5	400	656
	22	1.0/51.0	400	551
20	23	0.5/51.5	395	578
	24	0.5/51.5	400	559
	25	0.5/51.5	385	634
	26	1.0/51.0	390	541
	27	0.5/51.5	380	708
25	28	1.0/51.0	380	581
	29	0.5/51.5	370	680
	30	1.0/51.0	365	649
	31	0.5/51.5	390	605
	32	1.0/51.0	370	696
30	33	0.5/51.5	360	618
	34	1.0/51.0	365	641
	35	0.5/51.5	385	544
	36	1.0/51.0	390	584
	37	1.6/50.4	390	559

35

* Indicates dry coating weight

- 32 -

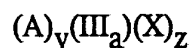
CLAIMS:

1. A coatable mixture including erodable filler agglomerates and a binder precursor, the mixture being suitable for use in making an abrasive article, the erodable filler agglomerates characterized by being a plurality of individual particles of water insoluble filler agglomerated by an agglomerating agent consisting essentially of water soluble filler and binder precursor, said water soluble filler being no more than 10 weight percent of the total weight of water soluble and water insoluble fillers.

10

2. Coatable mixture in accordance with claim 1 further characterized by said water insoluble filler being a material selected from the group consisting essentially of inorganic halide salts represented by the general formula

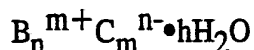
15



having a solubility in cold water of at most 10 gms/100 cc and mixtures thereof wherein:

- A = alkali metal ion, ammonium ion, or combinations thereof;
 20 $III_a = Al^{3+}, Ga^{3+}$, or combinations thereof;
 X = halide ion or combinations thereof;
 y = an integer from 1 to 10; and
 z = y + 3.

- 25 3. Coatable mixture in accordance with claim 1 further characterized by said water soluble filler being a material selected from the group consisting essentially of inorganic compounds represented by the general formula



having a solubility in cold water of at least 10 gms/100 cc, and mixtures thereof

30 wherein:

- B = Al, NH_4 , Ni, Zn, Fe, Cu, Mg, alkali metal, or combinations thereof;

- 33 -

C = HSO₄, SO₄, NO₃, PO₄, HPO₄, H₂PO₄, BF₄, or combinations thereof;

n = an integer from 1 to 5;

m = 5 - n; and

5 h = an integer ranging from 0 to 20.

4. Coatable mixture in accordance with claim 1 further characterized by the weight percent of water soluble filler no more than 2.5 weight percent of the total weight of said water soluble and water insoluble fillers.

10

5. A coated abrasive article characterized by including a cured version of the coatable mixture of claim 1.

6. A bonded abrasive article characterized by including a cured version
15 of the coatable mixture of claim 1.

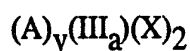
7. A nonwoven abrasive article characterized by including a cured version of the coatable mixture of claim 1.

20 8. Erodable filler agglomerates characterized by being a plurality of individual particles of water insoluble filler agglomerated by an agglomerating agent consisting essentially of water soluble filler and binder, wherein the water soluble filler is no more than 10 weight percent of the total weight of water soluble and water insoluble fillers.

25

9. Agglomerate in accordance with claim 8 further characterized by said water insoluble filler being a material selected from the group consisting essentially of inorganic halide salts represented by the general formula

30



- 34 -

having a solubility in cold water of at most 10 gms/100 cc, and mixtures thereof
wherein:

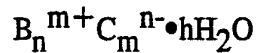
A = alkali metal ion, ammonium ion, or combinations thereof;

X = halide ion or combination thereof;

5 y = an integer from 1 to 10; and

z = y + 3

10. An agglomerate in accordance with claim 8 further characterized by
said water soluble filler being a material selected from the group consisting
10 essentially of inorganic compounds represented by the general formula



having a solubility in cold water of at least 10 gms/100 cc, and mixtures thereof
15 wherein:

B = Al, NH₄, Ni, Zn, Fe, Cu, Mg, alkali metal, or combinations
thereof;

C = HSO₄, SO₄, NO₃, PO₄, HPO₄, H₂PO₄, BF₄, or combinations
thereof;

20 n = an integer from 1 to 5;

m = 5 - n; and

h = an integer ranging from 0 to 20.

25

30

1 / 2

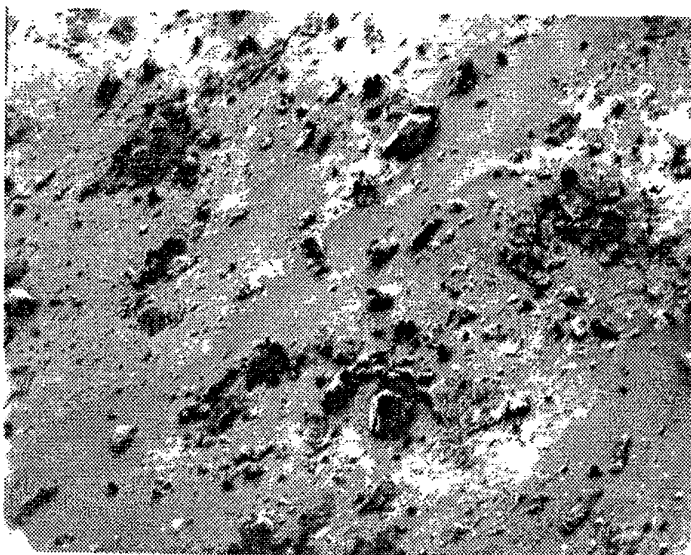


Fig 1

PRIOR ART

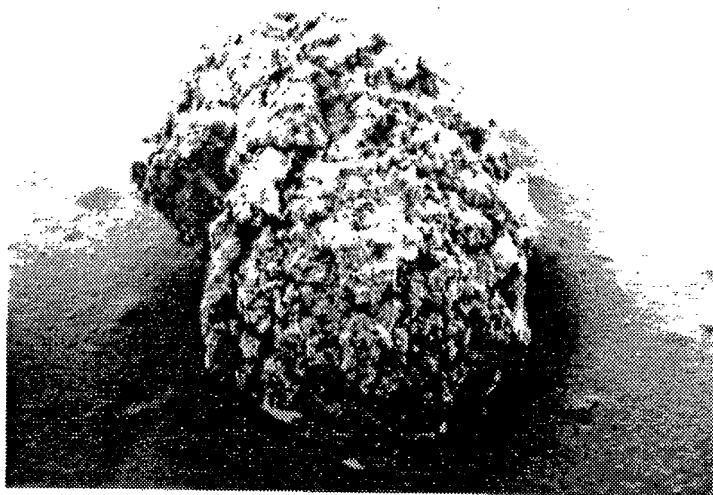


Fig. 2

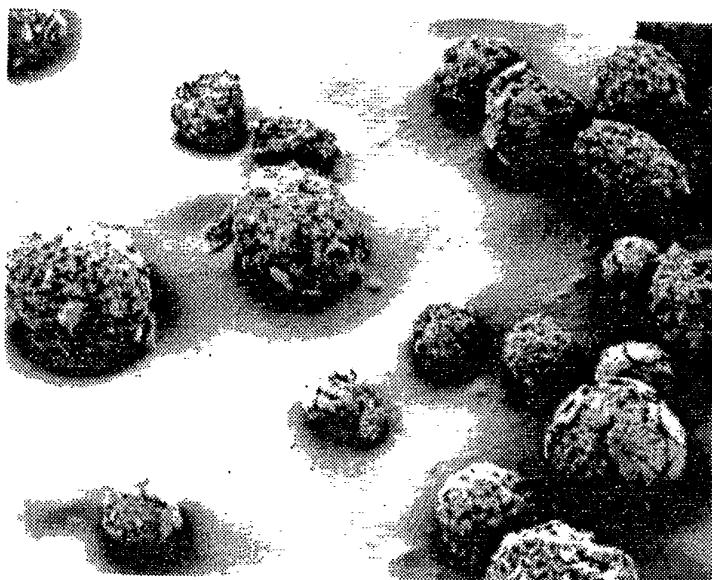


Fig. 3

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/00551

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C09K3/14; B24D3/28		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C09K ; B24D	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ^o	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
P,Y	US,A,5 104 424 (HICKORY) 14 April 1992 see column 4, line 47 - line 62; claims 1,3,4,15	1-3,5-9
Y	US,A,5 011 512 (WALD) 30 April 1991 cited in the application see claims 1,2,14,16	1-3,5-9
A	DE,A,2 600 353 (WAGNER) 21 July 1977 see claims 1,2,3	1-10
A	EP,A,0 078 896 (NORTON COMPANY) 18 May 1983 see claims 1,4,5,6	1-10
	-/--	
^o Special categories of cited documents : ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 10 MAY 1993		Date of Mailing of this International Search Report 25. 05. 93
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer NICOLAS H.J.F.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	DE,A,3 005 011 (SCHMIRGEL) 20 August 1981 see claims 1,5 -----	1-10
A	US,A,5 078 753 (BROBERG) 7 January 1992 see abstract; figure 1 -----	1-10

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9300551
SA 69634

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

10/05/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5104424	14-04-92	None	
US-A-5011512	30-04-91	CA-A- 1293862	07-01-92
DE-A-2600353	21-07-77	None	
EP-A-0078896	18-05-83	JP-A- 58082678	18-05-83
DE-A-3005011	20-08-81	None	
US-A-5078753	07-01-92	EP-A- 0480586	15-04-92