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ABRASIVES

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The present invention relates generally to the production of abrasives and more particularly to the production of grinding wheels for heavy duty use such as in snagging in the steel industry, and the like.

This application is a continuation-in-part of our application, Serial No. 503,795, filed April 25, 1955, and now Patent Serial No. 2,811,430.

In the production of abrasives a mixture of abrasive grains and a bond material including fillers, binder resin, plasticizers and other ingredients are combined and molded in various ways. The filler in a molded abrasive is believed to reduce cutting temperatures, prevent loading of the surface of the abrasive, and to otherwise improve cutting efficiency. The filler material usually employed is a finely ground or powdered natural mineral known as cryolite, having the general formula Na_3AlF_6 . Even though cryolite significantly improves the cutting efficiency of grinding wheels, in the grinding of stainless and alloy steels the performance of cryolite-filled grinding wheels has left something to be desired. Moreover, since cryolite is largely imported, its supply and price are subject to wide fluctuations in times of international crisis.

It is an object of this invention, therefore, to provide an abrasive article which contains an inexpensive, readily-available filler or fillers and which has an efficiency at least equal to that of cryolite.

Another object is to provide a filled abrasive article which will more satisfactorily grind stainless steel and other tough alloy steels. Still other objects and advantages of the present invention will be apparent, or will become apparent, in the more specific description of the invention to follow.

In accordance with the present invention an abrasive article is provided containing at least one filler selected from the class consisting of the alkali metal salts of sulfuric, hydrochloric and hydrobromic acid and mixtures of at least one of the latter salts with antimony sulfide. Most of these fillers or combinations of fillers are inexpensive and readily available in large quantities at all times. With combinations of the alkali metal salts and antimony sulfide in certain proportions, synergistic effects are noted, that is, the combination is much more effective than either of its components when used alone and an abrasive article is produced which is capable of cutting faster and which has longer life than heretofore known comparable abrasive articles manufactured for similar purposes. The abrasive articles of this invention are most effective in the cutting or grinding of stainless and alloy steels.

While we do not wish to be bound by theory due to the fact that the function of fillers is imperfectly understood, the following explanation is offered only because it appears to fit the facts as presently known. The stainless alloy steels and various of the other alloy steels high in total alloying ingredients, are characterized by their toughness and abrasion resistance. Consequently, grinding pressures and/or grinding times, must be increased to remove a given weight of metal, as compared to iron

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or mild steels. Consequently, the abrasive wheels wear away at an increased rate and temperatures generated at the metal-to-abrasive interface will usually be higher and may, in fact, be so high that a thin surface layer of the metal itself may be "burned," oxidized, or otherwise heat-modified to make it unsightly. The high temperatures may cause the heated metal to "load" the wheel and reduce its cutting efficiency. Likewise, the bond material, and particularly the filler content thereof, may be modified, volatilized or otherwise rendered ineffective at the temperatures obtained. We have observed that many materials which have melting points above about 1200° C. are not effective as fillers in abrasives for grinding the alloy steels. This might indicate that a good filler has a fluxing, protective or other function and that such function requires a liquefaction of the filler. Further support for the latter surmise is furnished by the observation that many of the most effective mixtures or combinations of fillers of the invention either are at or near their eutectic composition, or are compositions exhibiting lower melting points than one or both of its components used alone. It is believed that the sulfur of the sulfides is dissolved by the molten alkali metal salts to form a low melting fluxing composition that greatly facilitates grinding.

The abrasive articles of this invention may be any molded abrasive made from a mixture including abrasive grains and a bond material containing one or more of the above fillers and a resinous thermosetting binder material. The abrasive articles of this invention which are particularly effective are molded abrasives having a high density, that is, an abrasive article having a low percentage of void spaces (i.e. less than 15%). It is the latter type that is utilized in heavy duty grinding such as snagging. Any abrasive grain or mixture of grains may be employed including silicon carbide, boron carbide, tantalum carbide, tungsten carbide or other hard metal carbides; alumina such as emery, and including electric furnace fused alumina such as corundum, diamond grains, glass, quartz, garnet, etc.

The resinous binder material in the bond material must be curable, heat-hardenable or heat-convertible to form a hard, strong bond which will not readily deteriorate at elevated temperatures. An illustrative binder resin found particularly satisfactory in the abrasives of this invention is the fusible "B"-stage phenolic resins (phenolaldehyde or cresol-aldehyde resins which are available in either powdered or liquid form. If desired, the heat-convertible binder resin can be modified with small proportions of other resinous or rubbery materials such as the epoxy resins, vinyl resins including those of vinyl chloride, vinyl butyl and others, styrene-acrylonitrile resins, butadiene-acrylonitrile rubbers, and others and may contain varying proportions of cross-linking or curing agents such as hexamethylene tetramine, paraformaldehyde, and others. In some cases solvents or plasticizers such as furfuraldehyde, propylene sulfite, furfuryl alcohol, cresol, and others may be present in the bond mix, if desired. The bond mix may also contain, in addition to the fillers of this invention, any of the conventional fillers and other additive materials such as cryolite, feldspar, iron oxide, and others. If desired, the bond may also contain lime, and where furfuraldehyde is employed, the presence of lime is recommended.

The mixture of this invention which is molded may contain any operable ratio of abrasive to bond although, in general, for heavy duty grinding wheels the mixture will usually contain from about 54 to about 64% by volume of abrasive and from about 36% to about 46% by volume of the bonding material, it being understood that the bonding material so specified includes the binder resin, fillers, plasticizers and other added non-abrasive ingredients. An illustrative abrasive wheel mixture may

contain from about 54% to about 64% by volume of abrasive, from about 16 to about 26% by volume of binder resin or resins, from about 1% to about 4% by volume of lime, from about 8% to about 20% of total filler, and from 0 to 200 ml. of furfuraldehyde for every pound of powdered phenol-aldehyde resin, if the latter type is employed.

The above proportions used in the abrasives of this invention relate to the total volume of the finished abrasive. The proportion of filler, as related to the bonding material, can also vary considerably depending on the use to be made of the finished abrasive. Generally, the total filler content of the bonding material should range from about 5% to about 40% by volume, more preferably from about 10% to about 35%. These proportions include both the fillers of this invention and any other conventional filler or fillers which may be present. In general, any filler in addition to the filler of this invention should constitute no more than half the total filler and in no case should the proportion of the fillers of the present invention constitute less than about 2% by volume of the total bonding material.

In combination with antimony sulfide, any of the alkali metal salts of sulfuric, hydrochloric and hydrobromic acids may be employed as fillers in the abrasives of this invention including those of lithium, sodium, potassium, rubidium and cesium. Illustrative salts of this type include sodium sulfate, potassium sulfate, lithium sulfate, cesium sulfate (Cs_2SO_4), rubidium sulfate (Rb_2SO_4), sodium bromide, sodium chloride, potassium bromide, potassium chloride, and many others. All of the known alkali metal salts of these acids melt at temperatures below about 1100°C . and many of the more common salts of this type melt at temperatures between 400°C . to about 900°C . Of these, the sodium and potassium sulfates, sodium and potassium chlorides, and sodium and potassium bromides are most readily available, are less expensive and have been found to be very efficient fillers when used in admixture with antimony sulfide.

When antimony sulfide is added to the abrasive along with one or more of the alkali metal salts, a great improvement in the cutting efficiency of the resulting abrasive is usually noted. This is surprising since antimony sulfide, when used as a sole filler, either produces abrasives which are much poorer in cutting efficiency, or no more efficient than cryolite. As little as 5% to 10% antimony sulfide by volume, based on the total volume of alkali metal and antimony sulfide filler, significantly improves cutting efficiency. In most cases, as the proportion of sulfide is increased, large increases in cutting efficiency are realized until a point is reached where further increases in cutting efficiency are not obtained. For example, with mixtures of antimony sulfide and sodium sulfate, potassium chloride, sodium chloride, potassium bromide and sodium bromide, the maximum cutting efficiency is obtained with mixtures of about 50% antimony sulfide and 50% of the salt by volume, based on the total volume of the alkali metal and antimony sulfide fillers. When potassium sulfate is employed as the salt the maximum cutting efficiency occurs at mixtures of 25% antimony sulfide and 75% potassium sulfate, but the cutting efficiency is substantially at its maximum until a mixture of 75% antimony sulfide and 25% potassium sulfate is reached. Increases in antimony sulfide above about 75%, with the balance one of the salts above named, decreases the cutting efficiency. The cutting efficiency remains better than that obtainable with cryolite as the sole filler until the proportion of antimony sulfide is 85% of the total filler. Stated in terms of ratio, abrasives having snagging grinding characteristics superior to that obtainable with cryolite can be made with a ratio of antimony sulfide to alkali metal salt within the range of 5.6:1 to about 1:7.

The abrasive products of this invention can be made in any conventional manner. For example, the conven-

tional cold- or hot-pressing methods may be employed wherein the abrasive grains are first wet with furfuraldehyde or another plasticizer or solvent and the binder resin, fillers, and other dry, powdery or liquid ingredients then added to the wetted grains and mixed until homogeneous. The resulting damp mixture then is placed in either a hot or cold mold and pressed under high pressure to form a coherent "green" abrasive which is removed from the mold and heated in an oven to cure the bond. The displacement method disclosed in the co-pending application of John R. Gregor and Samuel L. Kistler, Serial No. 499,443, filed April 5, 1955, and now Patent Serial No. 2,860,961, may also be employed to advantage. In the latter method, dry, loose abrasive grains are placed in a suitable mold and a continuous layer of a fluid or fluidized bond mix applied to one exposed surface of the grain layer in the mold. Air is removed or is permitted to escape from the surface of the grain layer opposite the continuous bond layer to produce a flooding, directional movement of the bond layer toward the opposite surface to ensure complete filling of the voids. Gravity, vacuum, gas pressure, or centrifugal force may be applied to one side or the other of the abrasive layer to increase the speed of the directional movement of the bond. The abrasive is then baked to cure the bond. Any other method may be employed which is capable of producing a sound, compact, well-bonded abrasive article.

The invention will now be described in greater detail in connection with a number of illustrative specific examples. Unless otherwise specified in the examples, all proportions will be expressed as percent by volume.

A plurality of series of abrasive wheels were made by the cold pressing technique using a mixture containing 60% by volume of abrasive and approximately 38% to 40% by volume of bonding material including plasticizer. The bonding material had the following general composition, by volume:

Powdered B-stage phenol-formaldehyde resin	65
Lime	8
Filler	27

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To the dry abrasive grains there was first added 95 cc. of furfuraldehyde for every pound of binder resin to be employed. The liquid and abrasive were then mixed until a uniform consistency was obtained. The powdered bonding materials were first combined with 30 cc. of the equivalent of a neutral tar oil before being added to the somewhat moist mixture of abrasive and furfuraldehyde. Mixing was then resumed until a homogeneous mixture was obtained. Wheels were made from this mixture by cold pressing.

Each series of wheels included four control wheels which contained powdered cryolite as the sole filler. Four other control wheels were made employing antimony sulfide as the sole filler and four additional fillers were made employing the selected alkali metal salt as the sole filler. Four wheels were made containing a mixture of antimony sulfide and the selected alkali metal salt, constituting the entire filler, in the proportions of 75% alkali metal salt/25% antimony sulfide, 50% alkali metal salt/50% antimony sulfide, and 25% alkali metal salt/75% antimony sulfide by volume. In all cases the total filler constituted 27% by volume of the finished wheel. Each of these wheels, after curing, was then employed on a standard abrasive wheel grinding test machine in the grinding of Type 302 stainless steel. Each wheel was ground for a period of five minutes at the same pressure of about 250 lbs. per square inch, which is typical of pressures commercially employed in such grinding operations. The data presented in tabular form below represents the average of the results obtained with the four wheels:

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Sb₂S₃ with KCl

Filler	Wheel Wear, in. ³ /hr.	Steel Removal, lbs./hr.	S/W	Q
Cryolite.....	43.81	33.36	.761	82.8
K ₂ SO ₄	44.21	37.98	.859	103.5
75 K ₂ SO ₄ /25 Sb ₂ S ₃	31.60	29.94	.947	111.2
50 K ₂ SO ₄ /50 Sb ₂ S ₃	41.35	37.56	.908	110.4
25 K ₂ SO ₄ /75 Sb ₂ S ₃	38.68	33.90	.876	102.5
Sb ₂ S ₃	48.08	33.42	.695	71.9

Sb₂S₃ with Na₂SO₄

Filler	Wheel Wear, in. ³ /hr.	Steel Removal, lbs./hr.	S/W	Q
Cryolite.....	43.82	33.36	.761	82.8
Na ₂ SO ₄	55.20	39.96	.724	88.4
75 Na ₂ SO ₄ /25 Sb ₂ S ₃	48.43	38.58	.797	95.0
50 Na ₂ SO ₄ /50 Sb ₂ S ₃	44.03	34.86	.792	89.9
25 Na ₂ SO ₄ /75 Sb ₂ S ₃	47.68	36.96	.775	90.0
Sb ₂ S ₃	48.08	33.42	.695	71.9

Sb₂S₃ with KCl

Filler	Wheel Wear, in. ³ /hr.	Steel Removal, lbs./hr.	S/W	Q
Cryolite.....	43.82	33.36	.761	82.8
KCl.....	57.47	37.98	.661	75.6
75 KCl/25 Sb ₂ S ₃	40.59	35.46	.867	102.5
50 KCl/50 Sb ₂ S ₃	34.71	36.84	1.061	133.0
25 KCl/75 Sb ₂ S ₃	40.98	40.14	.980	121.9
Sb ₂ S ₃	38.15	26.58	.697	55.7

Sb₂S₃ with NaCl

Filler	Wheel Wear, in. ³ /hr.	Steel Removal, lbs./hr.	S/W	Q
Cryolite.....	43.82	33.36	.761	82.8
NaCl.....	54.92	38.52	.701	81.3
75 NaCl/25 Sb ₂ S ₃	44.06	40.74	.925	114.7
50 NaCl/50 Sb ₂ S ₃	47.03	43.62	.927	116.3
25 NaCl/75 Sb ₂ S ₃	44.12	38.70	.877	106.7
Sb ₂ S ₃	38.15	26.58	.697	55.7

Sb₂S₃ with KBr

Filler	Wheel Wear, in. ³ /hr.	Steel Removal, lbs./hr.	S/W	Q
Cryolite.....	48.15	35.40	.735	81.7
KBr.....	91.83	54.96	.600	87.4
75 KBr/25 Sb ₂ S ₃	76.65	59.88	.781	100.8
50 KBr/50 Sb ₂ S ₃	53.10	54.84	1.033	131.1
25 KBr/75 Sb ₂ S ₃	35.50	35.04	.987	121.1
Sb ₂ S ₃	30.83	23.64	.767	62.2

Sb₂S₃ with NaBr

Filler	Wheel Wear, in. ³ /hr.	Steel Removal, lbs./hr.	S/W	Q
Cryolite.....	48.15	35.40	.735	81.7
NaBr.....	54.96	41.22	.750	91.4
75 NaBr/25 Sb ₂ S ₃	60.35	50.52	.842	109.9
50 NaBr/50 Sb ₂ S ₃	45.34	42.66	.941	117.7
25 NaBr/75 Sb ₂ S ₃	34.85	33.48	.961	116.0
Sb ₂ S ₃	30.83	23.64	.767	62.2

The column headed Q represents a numerical evaluation of the over-all quality of the wheel and gives the Q number or quality number. The value of the quality number Q is expressed in the equation

$$Q = \frac{C_1}{W} - \frac{C_2}{S} + K$$

where W is the loss in weight of the wheel in cubic inches per hour, S is the pounds of steel or metal removed per

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hour and C₁, C₂ and K are constants. The value of these constants was determined by plotting the results of several hundred grinding tests using the conditions above specified with cryolite filled wheels and calculating the value of the constants from the plotted line. The constants C₁, C₂ and K so determined are 5549, 6000 and 136, respectively. The above Q values were all calculated using these constants.

It may be seen from an inspection of the above examples that the combination of antimony sulfide with each of the alkali metal salts illustrated gives S/W values and Q values which are greater than the corresponding values for cryolite alone, or antimony sulfide alone and in all cases except potassium sulfate, greater than the alkali metal salt alone. In making comparative grinding tests, many variables may affect the actual results obtained and in order to obtain reliable comparison figures it is necessary to utilize wheels which have been manufactured on the same day and cured at the same time or under identical curing temperature conditions. Moreover it is necessary to do all of the grinding of any one test on steel obtained from one batch. In all of the above tests these conditions were followed so that the relative figures within a specific test are meaningful but it should be understood that because of the variations which may occur in the steel being ground, the conditions of wheel manufacture or the conditions of operation of the testing equipment, it is not reliable to draw conclusions by comparing one set of test data against another. For example in the above data relatively wide numerical variations exist between the S/W ratios for the antimony sulfide control wheels employed in the potassium bromide and sodium bromide tests relative to similar wheels employed in the other tests and yet the data is reliable, on a comparison basis, in its own particular test.

What is claimed is:

1. An abrasive article comprising abrasive grains and a bonding material, said bonding material comprising a thermoset binder resin and a filler, at least one half of said filler consisting of at least one alkali metal salt of sulfuric, hydrochloric and hydrobromic acids in admixture with antimony sulfide, said admixed filler constituting at least about 2% by volume of the total bonding material and the ratio of antimony sulfide to said alkali metal salt being within the range of about 5.6 to 1 to about 1 to 7.
2. An abrasive article in accordance with claim 1 wherein said admixed filler consists of potassium sulfate and antimony sulfide.
3. An abrasive article in accordance with claim 1 wherein said admixed filler consists of potassium chloride and antimony sulfide.
4. An abrasive article in accordance with claim 1 wherein said admixed filler consists of potassium bromide and antimony sulfide.
5. An abrasive article in accordance with claim 1 wherein said admixed filler consists of sodium bromide and antimony sulfide.
6. An abrasive article in accordance with claim 1 wherein said admixed filler consists of sodium sulfate and antimony sulfide.
7. A cured molded abrasive article comprising abrasive grains, a thermoset phenolic binder resin, and a filler consisting essentially of a mixture of antimony sulfide and at least one alkali metal salt of sulfuric, hydrochloric and hydrobromic acids in which the ratio of antimony sulfide to said alkali metal salt is within the range of about 5.6:1 to about 1:7, said admixed filler constituting at least about 2% by volume of the total bonding material.
8. A cured molded abrasive article comprising abrasive grains, a thermoset phenolic binder resin and a filler consisting essentially of a mixture of antimony sulfide and at least one alkali metal salt of sulfuric, hydrochloric and hydrobromic acids and in which said antimony sulfide is present in an amount of from 5% to 85% by volume of

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the total mixed filler, said filler constituting at least about
2% by volume of the total bonding material.

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