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## SUPERSIZE FILM FORMING RESINS ON COATED ABRASIVES

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This invention relates to coated abrasive sheet material and is especially concerned with products having superior cutting efficiency and long life in steel sanding operations.

Abrasive products which are used to remove stock in metal abrading or grinding operations frequently fail because of a tendency of the abrading surface to lose its cutting effectiveness. In some instances the loss in cutting efficiency stems from fracture of the abrasive grains, and in other instances it occurs because the abrasive grains wear away by attrition. In either event, it appears that one of the major reasons for failure resides in the fact that a freshly exposed metal surface is extremely reactive. Such a fresh, or nascent, surface may react with the coated abrasive grain, forming a welded juncture which exerts an unusually severe shearing force on the grain. The welding phenomenon is rendered even more severe when the temperature of the surface being sanded is high.

Although the problems just described are serious when any abrasive material is used to remove metal stock, they are particularly acute when a coated abrasive is used as the abrading medium. In contrast to grinding wheels and similar molded abrasive products which can be renewed by removing the surface layer of dulled grains, coated abrasive material relies on essentially only one layer of abrading particles and hence little can be done to renew a dulled sheet. In an attempt to reduce friction between the abrasive grains and the metal surface being abraded, it has long been known to apply grease sticks, oils and similar lubricants from time to time during the abrading process. This technique is effective only to a limited degree, and the advantages are frequently offset by the attendant inconvenience, expense, and smudging of the workpiece. Similarly, water or oil floods at the point of grinding have proved inconvenient and expensive. Water necessitates the use of waterproof coated abrasive; oil causes a fire hazard; either requires special equipment.

A considerable amount of research has been carried out in an attempt to make grinding wheels more efficient by including in the bond a chemical which either per se or after decomposition at the grinding temperature reacts with the metal surface being abraded. For example, U.S. Patent No. 2,272,873 suggests including polyvinyl halides in a grinding wheel bond, and U.S. Patent No. 2,429,554 teaches the inclusion of aliphatic polymers such as chlorinated eicosane in either a grinding wheel bond or a sandpaper binder. The reasonable inference drawn from such prior art is that grinding wheels and coated abrasive products function in a similar manner, and a technique which improves the life of a grinding wheel must also improve the life of a coated abrasive product. Although we cannot say how effective metal-reactive, or corrosive, grinding aids are in improving the efficiency of a grinding wheel when included in the bond, we have found that the inclusion of such aids in the binder for a coated abrasive product is of essentially no value. It is possible that this ineffectiveness of grinding aids in coated abrasive bonds may be traced to the fact that, unlike grinding wheels, the adhesive bond is not usually worn away very much in an abrading process. It is also possible that

binders for coated abrasives are necessarily strong and heat-resistant, characteristics which drastically reduce, or even preclude, the availability of the grinding aid. Regardless of the reason, such grinding aids are not employed with coated abrasive products as far as we are aware.

We have now found a way in which conventional coated abrasive sheet material can be treated to render it more effective in the abrasion of metals. The treatment need not be renewed after it is initially applied, and the strength and effectiveness of the coated abrasive structure is in no way harmed. The purchaser of a coated abrasive is thus free from the bothersome step of having to apply some type of treatment to the abrading surface either constantly or at intervals throughout the abrading operation. Welding of the freshly exposed metal surface to the abrasive grains is greatly reduced, or even eliminated, thereby increasing the rate of cut and total life of the coated abrasive.

In accordance with our invention, we apply to surface of a coated abrasive sheet material to be used in metal sanding operations, an organic compound containing a chemically bound substituent which is displaced at the grinding temperature attained and which, in the presence of normal room humidity, is rapidly reactive with, or corrosive to, the metal being abraded. For the abrasion of steel with aluminum oxide particles we have found that a thin—in fact, almost microscopic—layer comprising an organic polymer having chemically bound atoms of chlorine, bromine, or divalent sulfur (which polymers respectively yield HCl, HBr, and H<sub>2</sub>S upon heating) is sufficient to improve the performance of the abrasive product by significant, and in some instances, astonishing amounts. Many of the polymers and compounds which we employ have been known for decades as grinding wheel adjuvants, but insofar as we are aware, they have never before been used to improve the performance of a coated abrasive product.

Temperatures are often very high at the interface between a coated abrasive and the metal which it is abrading, e.g., 1000° C. in the absence of a water or oil flood, but the effect is only momentary and the temperature gradient is abrupt. Thus, although most coated abrasive material would be quickly destroyed if heated in an oven to temperatures far below 1000° C., abrasive discs and belts are known to function effectively in the dry abrasion of steel, where such temperatures are reached. The organic compound which we apply to the surface of the coated abrasive is of a type which decomposes well below the temperature attained in grinding. Proposed compounds may be screened (1) by slowly heating a proposed compound to decompose it, as indicated by the presence of acidic vapors which change the color of moist blue litmus paper to red or precipitate a silver salt on moist paper impregnated with silver nitrate, (2) analyzing the gaseous decomposition products, and (3) checking the effect of these decomposition products on the coefficient of friction between a flat abrasive granule and the metal which is to be abraded. When, e.g., a grade 16 aluminum oxide grit with a wear flat was subjected to a load of 856 grams and spirally moved around a mild steel cylinder at 921 feet per minute, the coefficient of friction when a stream of HCl gas (a decomposition product of polyvinylidene chloride and polyvinyl chloride) was directed at the interface was less than half that attained under normal atmospheric conditions. Similar effects are found when H<sub>2</sub>S, HBr, and other materials disclosed hereinafter are employed. The reduction in friction demonstrates a rapid reaction between the metal surface and the gas supplied, and, as will be shown, substances which de-

compose to release such gases are effective grinding aids in the abrasion of steel.

Our invention will be better understood upon examination of the following examples, which are intended merely to illustrate the principle of our invention, but which are not intended to be restrictive. In the examples all parts are by weight unless otherwise noted.

#### Example I

Two endless coated abrasive belts 3 inches wide and 84 inches long were fabricated from coated abrasive sheet material having hide glue make and sandsize adhesive and grade 60 aluminum oxide mineral. The control belt was made from a standard commercial coated abrasive material; the other belt was made from the same coated abrasive material which had, however, first been "supersized" (i.e., additionally coated) with a tetrahydrofuran solution of polyvinyl chloride ("Geon" 101) to apply 0.98 milligram of polyvinyl chloride per square inch. Upon heating to 200° C. this polymer gave off HCl. The performance of each belt was evaluated by mounting it, in turn, on a conventional "backstand" machine where it was entrained over a 14-inch diameter flat rubber contact wheel driven at 7,180 surface feet per minute, while flat cold rolled steel bars were forced against it and reciprocated slowly. The endpoint was arbitrarily set as the time when the rate of cut fell below 7.5 grams per minute. The control belt cut 306 grams of cold rolled steel in 15 minutes, while the supersized belt of this example cut 348 grams in 18 minutes.

#### Example II

Four 3" x 84" coated abrasive endless belts having phenol-formaldehyde make and sandsize adhesives and grade 24 aluminum oxide were obtained. Two belts were retained as controls while the other two were coated with the same solution of polyvinyl chloride used in Example I. Evaporation of the solvent left a continuous film of the polymer weighing approximately 1.7 milligrams per square centimeter. These belts were evaluated on the same equipment described in Example I. The two control belts lasted 28 minutes, averaging 730 grams of steel removed during that period of time. The two polyvinyl chloride-treated belts lasted 35 minutes during which time they removed an average of 1,426 grams of steel. It is surprising that such a minute amount of grinding aid can have such a profound effect, but it is even more surprising that the presence of as little as 1/2 the quantity of polyvinyl chloride employed in this example significantly improves the performance of a coated abrasive product used to sand steel. It would be supposed, especially in view of the prior art, that such a modest amount of material would, if effective at all, quickly be removed during the course of abrading.

#### Example III

Two 3" x 84" coated abrasive belts of the same construction described in Example II, except that the mineral was grade 50 aluminum oxide, were obtained. One of these belts was retained as the control while the other was treated with 6.7 milligrams per square centimeter of a resin made by blending 63 parts of "Polyglycol 166-1150" and 37 parts of "Mondur CB-75," after which the sheet was cured for 20 hours at 230° F. "Polyglycol 166-1150," obtained from the Dow Chemical Co., is a polyepichlorhydrin having a molecular weight of about 1150. "Mondur CB-75" is a 75% ethylacetate solution of the reaction product of 1 mol of trimethylol propane and 3 mols of toluene 2,4-diisocyanate. Upon severe heating, this polymer yielded HCl. In 22 minutes under the test conditions described in Example I the control belt cut 584 grams of steel, while the treated belt cut 674 grams.

#### Example IV

A coated abrasive belt identical to the control belt described in Example III was supersized with 8.5 milli-

grams per square centimeter of a resin made by blending 62 parts of "EpiRez 5161," 27 parts of hexahydrophthalic anhydride and 11 parts of "HET" anhydride, after which the structure was cured for 2 1/2 hours at 225° F. Upon severe heating, this supersize material gives off HCl. "EpiRez 5161," obtained from the Jones-Dabney Co., is the diglycidyl ether of tetrachlorobisphenol A. "HET" anhydride, obtained from Hooker Chemical Co. is 1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)-5-heptane-2,3-dicarboxylic anhydride.

When employed on the same test described in the preceding examples, the control belt cut 931 grams of steel in 34 minutes while the treated belt cut 1,334 grams of steel in the same time under identical operating conditions.

The "HET" acid corresponding to the "HET" anhydride used in this Example IV may also be reacted with an aliphatic glycol to provide a polyester resin containing chemically bound chlorine atoms. This polyester may then be applied as a supersize coating on a conventional coated abrasive sheet material used to abrade steel with noticeable improvement in performance over that of an untreated coated abrasive.

#### Example V

A grade 50 coated abrasive belt 3" x 84" and similar in construction to that employed in Example III was treated with 3.1 milligrams per square centimeter of a polyester resin containing chemically bound divalent sulfur. This resin yields H<sub>2</sub>S upon heating. The polyester was prepared by blending equal parts by weight of (1) the reaction product of 2.18 mols of mercapto succinic acid and 2 mols of neopentyl glycol, prepared using the water-toluene azeotrope method, and (2) N,N'-bisethylethyleneisosebacamide. The treated structure was cured for 2 hours at 220° F. and tested in the same manner described in Example I. In 18 minutes an untreated control belt cut 492 grams of steel, while the belt of this example cut 568 grams of steel in the same length of time.

#### Example VI

A conventional 9 1/8" diameter coated abrasive disc having grade 60 aluminum oxide mineral bonded to .030 inch vulcanized fiber with phenol formaldehyde make and size resin, was supersized with 11.6 milligrams per square centimeter of a resin made by reacting equal parts by weight of 1-epoxyethyl-3,4-epoxycyclohexane and "HET" anhydride, after which the structure was cured for 12 hours at 225° F. The disc was mounted on a rigid circular backup plate where it was driven at 3,450 r.p.m. The edge of a 0.074 inch thick circular plate of cold rolled steel was forced against the abrasive surface of the disc at approximately 90° with a force of about 5.9 lbs. and driven at a rate of 2 r.p.m. In 8 minutes the disc cut 71.8 grams of steel, while a conventional disc, i.e., identical except that it was not supersized, cut 45.2 grams of steel in the same length of time.

#### Example VII

To the surface of a grade 60 coated abrasive disc of similar construction to the control disc described in Example VI was applied a solution of polyvinylidene chloride ("Saran F-120," a product of the Dow Chemical Co.), and the solvent evaporated to leave a continuous film weighing 3.4 milligrams per square centimeter. In a test similar to that described in Example VI this disc cut 91.8 grams of steel in 8 minutes while a control disc cut only 70.2 grams of steel in the same length of time.

#### Example VIII

A coated abrasive disc similar to the control disc described in the Example VI was coated with a dilute solution of polyvinyl bromide and the solvent evaporated to leave a continuous film weighing approximately 3.4 milligrams per square centimeter. Polyvinyl bromide yields

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HBr when heated. In the test described in the preceding example this disc cut 94.2 grams of steel in 8 minutes while an untreated disc of the same construction cut only 70.2 grams of steel in the same length of time.

#### Example IX

A conventional coated abrasive disc having the same construction as the control disc described in Example VI was coated with a dilute solution of a chlorinated coumarone-indene resin marketed by the Neville Chemical Company and the solvent evaporated to leave a continuous film weighing 3.4 milligrams per square centimeter. In the disc test described in Example VI this disc cut 95.2 grams of steel in 8 minutes while an untreated disc cut only 70.2 grams of steel in the same length of time.

#### Example X

Four conventional coated abrasive discs having the same construction as the control disc described in Example VI were coated with a dilute solution of a vinyl chloride:vinyl acetate copolymer ("Vinylite VAGH," sold by the Bakelite Division of Union Carbide Co.), and the solvent evaporated to leave a continuous film weighing approximately 3.6 milligrams per square centimeter. In a disc test similar to that described in preceding examples except that a stainless steel workpiece was employed, the four treated discs removed an average of 42.2 grams of stainless steel in 8 minutes, and four untreated but otherwise identical discs removed an average of 30.6 grams of steel in the same length of time.

#### Example XI

Four conventional coated abrasive discs having the same construction as the control disc described in Example VI were supersized with a dilute solution of a Thiokol polymer ("EC801," sold by Minnesota Mining and Manufacturing Co.), and the solvent evaporated to leave a continuous film weighing approximately 5.2 milligrams per square centimeter. In the test described in Example X, the four supersized discs removed an average of 36.6 grams of stainless steel in 8 minutes, while four control discs removed an average of 30.6 grams in the same length of time.

An attempt has been made in the preceding examples to describe a wide variety of polymeric supersizes for conventional coated abrasive products which serve to improve the performance in the abrasion of various steels. We have found that polyvinyl chloride and polyvinylidene chloride, both of which contain a high percentage of chlorine and decompose at comparatively low temperatures, are particularly effective. It will be apparent to those skilled in the art that a large number of other polymeric materials can also be made to function satisfactorily. Thus, for example, the following polymers may also be used with substantial improvement noted in the treated coated abrasive: polyvinyl mercaptan, poly alpha-chloroacrylate, poly alpha-bromoacrylate, chlorinated rubber, rubber hydrochloride, polychloroprene, poly 2-chloroethyl acrylate, poly 2-bromoethyl acrylate, polychlorostyrene, polybromostyrene, poly N-(beta-mercaptopropyl) vinyl amine, and resinous coatings based on "HET" acid polyesters, and diglycidyl ethers of tetrabromobisphenol A epoxy resins.

Although we prefer to use polymeric materials which themselves are suitable film formers, and hence can be applied per se, to insure uniformity of treatment and ease of application, it is possible to use other polymeric materials as carriers for either film-forming or non-film forming organic heat-decomposable grinding aids. Care must be taken in this event, however, to insure that the carrier is not itself so stable that it inhibits the effectiveness of the sanding aid. In addition, the quantity of carrier employed should be held to the minimum which will retain the sanding aid at the working surface without masking its effect.

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It will be noted from the preceding examples that extremely small amounts of the polymeric grinding aids are effective in producing improved results. Although it appears that the presence of chemically bound chlorine, bromine, or divalent sulfur in any heat-unstable polymer we have evaluated renders it satisfactory as a supersize for improved metal sanding coated abrasive products, the exact degree of performance cannot be predicted with certainty. Thus, one polymer is not necessarily more desirable than another because of a higher content of active element. Nor, surprisingly, does the application of increased amounts of an effective supersize continue to improve metal-sanding performance proportionally. As a matter of practice, the upper limit of polymeric grinding aid applied is determined primarily by economy and a desire not to have so much supersizing material present that the ability of the abrasive grains to function is limited because they are buried. Generally speaking, coarser grade products may employ more metal-reactive supersize than finer, or polishing grades.

Although coated abrasive surfaces treated in accordance with our invention are apparently effective at almost any operating pressure, we believe that the greatest utility for such treated materials will lie in the moderate to severe grinding pressure applications typified by the wide belt grinding of sheet steel. Likewise, although these grinding aids will improve the performance in any dry ferrous metal abrading operation, the greatest improvement is noted in those operations where failure of the coated abrasive product normally occurs because of dulling or glazing, rather than mineral loss.

Having now described our invention and illustrated its use with the aid of numerous examples, what we claim is as follows:

1. A coated abrasive article in which a layer of aluminum oxide granules is firmly bonded to a sheet backing by at least one adhesive selected from the class consisting of hide glue and phenol-formaldehyde resin, said article having outstanding ability to abrade a steel surface effectively under heavy pressure for extended periods of time while resisting the normally occurring welding of the freshly exposed steel surface to said granules and being characterized by the presence at the abrading surface of said article of a layer consisting essentially of a heat-decomposable film-forming polymer selected from the class consisting of polymers of vinyl chloride and polymers of vinylidene chloride, said adhesive being present in such quantity that the mechanical strength of said coated abrasive article is essentially the same as if said film-forming polymer were not present.

2. The product of claim 1 wherein said film-forming polymer is polyvinyl chloride.

3. The product of claim 1 wherein said film-forming polymer is polyvinylidene chloride.

4. The product of claim 1 wherein said film-forming polymer is a copolymer of vinyl chloride and vinyl acetate.

5. A coated abrasive article having outstanding ability to abrade a steel surface effectively under heavy pressure for extended periods of time while resisting the normally occurring welding of the freshly exposed steel surface to the abrading surface thereof, said article comprising a sheet backing, a hardened make adhesive and a hardened sandsize adhesive firmly bonding aluminum oxide granules to said backing, and, at the exposed abrading surface of said article, a supersize coating which differs in composition from said sandsize adhesive and which consists essentially of a heat-decomposable film-forming organic polymer containing a chemically bound substituent which can form the anion of an acid selected from the class of HCl, HBr, and H<sub>2</sub>S, said make and sandsize adhesives being present in such quantity that said supersized coating contributes essentially nothing to the mechanical strength of the coated abrasive product, said polymer being selected from the class consisting of

polyvinyl chloride; polyvinylidene chloride; vinyl chloride-vinyl acetate copolymer; polyvinyl bromide; reaction product of polyepichlorohydrin and trimethylol propane; toluene 2,4-diisocyanate polymer; reaction product of tetrachlorobisphenol A, 1,4,5,6,7-hexachlorobicyclo-(2,2,1)-5-heptane-2,3-dicarboxylic anhydride and hexahydrophthalic anhydride; reaction product of 1-epoxyethyl-3,4-epoxycyclohexane and 1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)-5-heptane-2,3-dicarboxylic anhydride; chlorinated coumarone-indene resin; reaction product of mercaptosuccinic acid: neopentyl glycol polyester and N,N'-bisethylenisosebacimide; and Thiokol.

6. The product of claim 5 wherein said film-forming polymer is polyvinyl chloride.

7. The product of claim 5 wherein said film-forming polymer is polyvinylidene chloride.

8. The product of claim 5 wherein said film-forming polymer is a copolymer of vinyl chloride and vinyl acetate.

9. A coated abrasive article having outstanding ability to abrade a steel surface effectively under heavy pressure for extended periods of time while resisting the normally occurring welding of the freshly exposed steel surface to the abrading surface thereof, said article comprising a sheet backing, a hardened make adhesive and a hardened sandsize adhesive firmly bonding aluminum oxide granules to said backing, and, at the exposed abrading surface of

said article, a supersize coating which differs in composition from said sandsize adhesive and which consists essentially of a heat-decomposable film-forming organic polymer containing a chemically bound substituent which can form the anion of an acid selected from the class of HCl, HBr, and H<sub>2</sub>S, said make and sandsize adhesive being present in such quantity that said supersized coating contributes essentially nothing to the mechanical strength of the coated abrasive product.

#### References Cited by the Examiner

##### UNITED STATES PATENTS

|           |         |                 |          |
|-----------|---------|-----------------|----------|
| 2,236,597 | 4/1941  | Hatch           | 51—298.1 |
| 2,269,415 | 1/1942  | Netherly et al. | 51—295   |
| 2,281,558 | 5/1942  | Cross           | 51—295   |
| 2,327,846 | 8/1943  | Kistler         | 51—295   |
| 3,030,251 | 4/1962  | La Bore et al.  | 51—297   |
| 3,058,819 | 10/1962 | Paulson         | 51—295   |

##### FOREIGN PATENTS

|         |        |            |
|---------|--------|------------|
| 118,147 | 3/1944 | Australia. |
|---------|--------|------------|

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