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④ Coated abrasive.

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③ Proprietor: **NORTON COMPANY**
1 New Bond Street
Worcester Massachusetts 01606 (US)

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⑦ Inventor: **Ibrahim, Mohamed Mostafa**
28 Ashley Drive
Ballston Lake New York (US)

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⑦ Representative: **Baillie, Iain Cameron et al**
c/o Ladas & Parry Isartorplatz 5
D-8000 München 2 (DE)

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BE-A- 494 833
DE-A-1 646 824
DE-A-2 226 744
DE-A-2 720 829
DE-C- 818 863
FR-A-2 330 504
US-A-1 591 001
US-A-2 983 593

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Description

The present invention relates to coated abrasives which consist of flexible backings to which are adhered a plurality of abrasive grit particles on at least one side. Coated abrasives are used primarily for the shaping, dimensioning, or surface finish alteration of other material objects known generally as workpieces. Small particles of material removed from the workpieces and/or shed from the coated abrasives during working are collectively called "swarf". In many cases, the swarf tends to wholly or partially adhere to the surface of the coated abrasive, eventually loading or clogging its abrasive surfaces and rendering it unsuited for further use. This invention relates particularly to coated abrasives which are specially resistant to such failure by loading.

A common commercial practice for the preparation of coated abrasives which resist loading in the sanding of paints, primers, wood sealer coats, and a wide variety of other finishing compositions used on workpieces is essentially that described in U.S. Patent 2,768,886. This patent describes the preparation of coated abrasives which have a final grit-side surface coating of unfused metallic soaps applied preferably from dispersion of such soap in a volatile liquid. The application of this metallic soap is done as a separate coating step in addition to the normal making and sizing coating steps which are customarily used for achieving adherence of the abrasive grits to the backing. In some cases, it may be possible to prepare products with adequate properties without using a sizing adhesive. The need for an additional coating operation compared with most other coated abrasive imposes labor and material costs which it would obviously be advantageous to avoid.

Since the publication of the above patent, there have been several other patents directed to other types of "third" coatings (i.e., coatings in addition to the two normal making and sizing ones) which would achieve loading-resistant coated abrasives. Examples include polyvinyl-acetate as disclosed in Canadian Patent 931,767, polytetrafluoroethane and mixtures thereof as disclosed in U.S. Patent 3,042,508, and mixtures of thermosetting resins, elastomers, and metallic soaps as disclosed in U.S. Patent 3,619,150.

U.S. Patent 3,043,673 teaches the use of oxy-containing compounds either in a third coat or in the conventional sizing coat of a coated abrasive, together with an exceptionally high ratio of binder adhesive to grain, as an effective means for increasing the resistance of coated abrasive to loading in the finishing of leather and similar materials. The oxy compounds specified in this patent are all neutral organic compounds not expected to ionize in water solution. U.S. Patent 3,089,763 teaches the use of polyoxyalkylene compounds in the size of coated abrasives, and one of the objects stated is to reduce loading. However, the teaching of this U.S. Patent is restricted to sizing compositions in which the principal constituent is an amine catalyzed phenolic resin.

DE—A—1 646 824 and DE—A—2 226 744 teach the use of phosphoric acids and glasses, phosphate esters, and phosphoric metal salts in the adhesive of coated abrasives as grinding aids to achieve an improved grinding of easily passivated metals such as titanium and stainless steel. Amounts of phosphorus compounds at least equal in weight to the remainder of the adhesive used are taught for this purpose. U.S. Patent 1 591 001 teaches the use of more than 10% by weight of phosphate salts and/or esters in waterproof adhesives for coated abrasives in order to make the coated abrasives fire-proof. None of these prior art references, however, teaches that the loading resistance of coated abrasives can be improved by the presence of phosphorus compounds, and because the adhesives taught by these references did not contain any glue or amino resins, loading resistance could not be achieved by the presence of phosphorus compounds alone.

Many prior art references, such as U.S. Patent 2 983 593, teach the general use of amino resins or glue as adhesives for coated abrasives. While it might be within the general teachings of the prior art to add phosphorus compounds to such adhesives as grinding aids or fireproofing agents, as taught by the references noted immediately above, there is no known instance of such use in the prior art, nor any teaching known to the applicant of achieving improved loading resistance for a coating abrasive having amino resins or glue as its outermost adhesive layer by any additive whatever.

It is a primary object of this invention to provide coated abrasives which are as resistant to loading as products with metallic soap third coats but which do not require an actual third coating.

In accordance with the present invention there is provided a coated abrasive article comprising a flexible backing, a plurality of abrasive grit particles dispersed over the area of at least one surface of said backing, and at least one layer of adhesive bond material adhering said abrasive grit particles to each other and to said backing, characterized by the fact that the outermost layer of said adhesive bond material comprises:

- (a) animal glue, or a cured amino resin, or a mixture thereof in an amount of at least 40% by weight of the total adhesive bond material, exclusive of any filler; and
- (b) at least 0.74 grams per square meter, but not more than 10% of the total weight of the total adhesive bond material in said outer layer, exclusive of any filler, of an additive which is
 - (1) a partial ester of phosphoric acid,
 - (2) a salt of a partial ester of phosphoric acid with an amine,
 - (3) a tetraorganylammonium salt, or
 - (4) a soluble mixture thereof.

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Typical examples of (b) would be the triethanolamine salt of mono- or di- decylphosphate or stearamidopropyl- β -hydroxyethylammonium nitrate.

In the studies which led to this invention, use was made of conventional coated abrasive backings, maker adhesives, and abrasive grits. The invention is applicable to any such products containing any such constituents, including the full range of grit sizes of normal commercial practice, comprising at least those with numerical designations of size from 12 to 600 as defined by the ANSI standard B74.18-1977. As is known to those skilled in the art, suitable constituents include but are not limited to papers of weights varying from 50 to 300 grams per square meter (gm/m²), suitably prepared (finished) cloth of a wide variety of types, and vulcanized fiber. Grits can be synthetic fused alumina, silicon carbide, garnet, zirconia alumina, emery, flint, or other materials, and maker adhesives can be film-forming starches, animal hide glue, amino resins, etc.

The additives investigated which had detectable effect in reducing loading when used in the size coat are listed in Table 1. These additives were most effective when used with amino resins such as urea-formaldehyde or melamine-formaldehyde. Such amino resins could be mixed in up to equal parts by weight with phenol-formaldehyde resins, one amino resin could be mixed with others, and any of the resins or mixtures could be filled with finely divided solids such as calcium sulfate, walnut shell flour, or any of the other well-known fillers used in the manufacture of coated abrasives. Suitable types of naturally derived glue can also be used as the size, although the product performance with glue sizes will normally not be as effective as with resin size, as is true in the absence of the additives disclosed here.

Still other conventionally known materials, such as pigments or dyes, diluents for reducing viscosity, anti-foam agents, etc. may be used together with the additives of this invention when needed or desired. No adverse interactions between such materials and the additives of this invention have been noted. A particularly important class of conventional components in amino resin adhesive formulations are the oxyamines useful for craze resistance as taught by Duke in U.S. Patent 2,983,593, the entire specification of which is hereby incorporated herein by reference. Use of adhesive compositions as taught by Duke, in combination with the additives of my invention, is preferred.

TABLE 1
Additives which improve loading resistance of amino resin and glue sizing adhesives for coated abrasives

30	Trade mark name of additive	Supplier	Chemical characterization*
35	Zelec NE	Group A E. I. duPont	Fatty alcohol phosphate, neutralized
	Zelec NK	E. I. duPont	Fatty alcohol phosphate
40	Monafax L-10	Mona Industries	Mixture of mono- and di-phosphate esters derived from ethylene oxide based surfactants
	Monafax 786	Mona Industries	Same as Monafax L-10
45	Emphos PS-400	Group B Witco chemical	Complex organic phosphate esters
	Monafax 785	Mona Industries	Same as Monafax L-10
50	Monafax H-15	Mona Industries	Same as Monafax L-10
	Cyastat SN Cyastat SP	Group C American Cyanamid American Cyanamid	Stearamidopropyl- β -hydroxyethyl- dimethylammonium salts; nitrate for SN, dihydrogen phosphate for SP
55	E-1373	Calgon Corporation	Mixture of Dimethyldiallylammonium chloride and Methylolacrylamide

60 *As specified by the supplier

It should be noted that some of the additives shown in Table 1 are acidic and thus capable of catalyzing the cure of amino resins. However, such a practice would incur risk of shortened pot life of the amino resin, compared to use of the catalysts taught by Duke. Thus it is usually preferable in practicing my invention to neutralize the additive, if it is acidic, with a suitable amine or ammonium hydroxide before adding it to an

amino resin adhesive formulation. When this is done, the resin adhesive with my additive can be cured with the same time and temperature program as is useful for the same resin without the additive. It is convenient to use one of the oxyamines taught by Duke to neutralize the additive of my invention if needed.

For example, Zelec NE, which is neutral as supplied, could be added directly to a conventional formulation such as Example III of Duke patent, after all the other ingredients listed there are mixed together. On the other hand, Zelec NK, which is acidic, should first be neutralized, conveniently with 2-amino-2-methylpropanol, in a separate container, and the neutralized mixture then added to such a conventional formulation after all other ingredients had been added. All preceding and subsequent stages of manufacture of the coated abrasive may be carried out in a conventional manner.

10 The minimum amount of additive to give a useful loading resistance effect was found to be that corresponding to a mass of 0.74 grams per square meter. An amount more than 10% by weight of the total sizing adhesive used is generally not desirable, because of probable decrease in the heat-distortion resistance of the sizing adhesive, with resultant danger of reduction of grinding effectiveness. In general, the workable range is from 0.74 to 13.3 grams per square meter of additive, and the preferred range is from 15 1.2 to 3.5 grams per square meter. This can be conveniently achieved in most cases by using the additive at a level of 3—5% by weight of the resin or glue used.

15 The additives listed in Table 1 all mixed readily with amino resins or glue suspensions to give liquid mixtures which were uniform as far as could be noted visually, although in some cases there was a hazy or milky appearance to the mixture, indicative of dispersion rather than true solution. There was no direct 20 evidence during processing of any tendency of the adhesive mixtures containing the additives to develop inhomogeneities under normal conditions of coating, drying, or cure. However, it is expected from the chemical nature of the preferable additives, which contain both ionic bonds and at least one long organic chain in each molecule, that such additives may effectively reduce the surface tension of most liquid adhesives into which they are mixed. If such reduction in surface tension actually occurs, the well-known 25 Gibbs equation for such surface active species predicts that the surface active component(s) will spontaneously distribute themselves at equilibrium so as to form a surface layer enriched in the surface active component. This spontaneous concentration of additive in the surface layer may explain why the minimum amount of additive required to obtain a detectable increase in loading resistance was found to be related to the area of the coated abrasive product rather than to the volume of adhesive.

30 Size height levels for products coated with sizes containing the additives taught herein should generally conform to those for conventional products which are not to receive an additional third coating. In any case, suitable levels can easily be determined if necessary by those skilled in the art of manufacturing coated abrasives.

35 Table 2 illustrates examples of specific products prepared according to the methods of this invention. The group of the four additives listed in Table 1 as Group A all appeared to be approximately equal in their ability to induce loading-resistance when added to amino resin sizes. Products with these additives in the size coat were tested in sanding of a wide variety of paints, metal primers, enamels, lacquers, varnishes, etc. and found in general to have longer useful lives than previous standard commercial products made for sanding such workpieces. (Such commercial products normally have a third coating 40 containing primarily zinc stearate or some other similar metallic soap.) The other additives shown in Table 1 are listed in groups of decreasing effectiveness in imparting loading-resistance to the size adhesives.

45 In this specification and in the claims below, the term "organyl" is used to include any chemical group which could be formed by the breaking of one valence bond in an organic compound. Thus organyl includes the groups normally designated as alkyl, alkenyl, alkynyl, aryl such as phenyl, and combinations of and substitutions on the other simple groups, as well as a wide variety of others. The term "long organyl" refers to an organyl group which comprises at least eight carbon atoms bonded linearly to each other. The linear bonding may include double or triple as well as single carbon-carbon bonds. The term "layer" in the 50 description of a body of adhesive material is to be considered to include any substantially continuous body of material of substantially uniform composition, with a projected area covering substantially all of the area of an abrasive backing. Because of the presence of abrasive grit particles in a coated abrasive, the layers of adhesive used in the construction thereof are expected to have very irregular outer surfaces rather than the smooth parallel surfaces normally suggested by the word layer in ordinary usage. As an example, the maker and sizer adhesive coats noted above in the brief description of the normal manufacturing process for a coated abrasive would constitute layers in the finished product, as would any separate coat of metallic 55 soap intended to confer loading resistance. It should be further noted that substantial uniformity of composition of an adhesive layer is intended to include any natural surface enrichment of a surface active material incorporated into the adhesive layer when it is applied in liquid form. Also, substantial continuity of an adhesive is not violated by the presence of normal flex cracks in a coated abrasive.

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TABLE 2
Specific examples of loading resistant coated abrasives

5	Marker adhesive			Abrasive grits			Sizing adhesive		
	Backing	Type	Gm/m ²	Type	Grit size	Gm/m ²	Total Gm/m ²	Main type	Additive
10	B1	M1	15	G1	360	44	30	S1	Zelec NE 1.2
	B1	M1	15	G2	320	44	30	S1	Monafax L-10 1.2
15	B1	M1	19	G3	220	77	62	S1	Zelec NE 2.5
	B1	M2	12	G4	220	40	30	S1	Zelec NK 1.2
20	B2	M1	22	G2	180	98	62	S1	Monafax 785 2.5
	B1	M1	22	G5	180	53	30	S2	Monafax 786 1.2
25	B3	M3	118	G6	80	129	133	S2	Cyastat SN 5.3
	B1	M1	26	G1	120	138	77	S3	Emphos PS-400 3.1
30	B4	M1	56	G1	220	115	81	S1	E-1373 3.3

*As listed in Table 1.

30 Symbol keys

Gm/m² indicates dried grams of item indicated per square meter of coated abrasive.

Backings:

B1 is 68 gm/m² Kraft paper (Style 28729 from Kimberly-Clark); B2 is slightly heavier Kraft paper (Style 35 54729 from Kimberly-Clark); B3 is 130 pound basis weight (220 gm/m²) N cylinder paper from James River; B4 is cotton jeans cloth finish 207CC from Norton Co.

Makers:

M1 is 82 millipoise animal glue; M2 is Ucar 131 latex from Union Carbide; M3 is urea-formaldehyde resin GPX-J1-6 from Georgia-Pacific.

Abrasive grits:

G1 is a type SWPL alumina from Treibacher USA, Inc.; G2 is type FRPL alumina from Treibacher; G3 is type 57 Alundum from Norton Co.; G4 is garnet from Barton Mines; G5 is silicon carbide from Norton Co.; G6 is a mixture of type 57 Alundum and NZ Alundum from Norton Co. in a volume ratio of 6:4.

Sizer adhesives:

S1 is urea-formaldehyde resin type Beetle 7238-20 from American Cyanamid; S2 is urea-formaldehyde resin type GPX-J1-6 from Georgia-Pacific; S3 is a mixture of Beetle 7238-20 and phenolic resin 2535 from 50 Varicum Chemical Co. in equal proportions by weight.

Claims

55 1. A coated abrasive article comprising a flexible backing, a plurality of abrasive grit particles dispersed over the area of at least one surface of said backing, and at least one layer of adhesive bond material adhering said abrasive grit particles to each other and to said backing, characterized by the fact that the outermost layer of said adhesive bond material comprises:

(a) animal glue, or a cured amino resin, or a mixture thereof in an amount of at least 40% by weight of the total adhesive bond material, exclusive of any filler; and

60 (b) at least 0.74 grams per square meter, but not more than 10% of the total weight of the total adhesive bond material in said outer layer, exclusive of any filler, of an additive which is

- (1) a partial ester of phosphoric acid,
- (2) a salt of a partial ester of phosphoric acid with an amine,
- (3) a tetraorganylammonium salt, or
- (4) a soluble mixture thereof.

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2. A coated abrasive according to claim 1, characterized by the fact that said additive in the outermost adhesive layer has at least one long organyl group per molecule.
3. A coated abrasive according to claim 1 or 2, characterized by the fact that the outermost layer of adhesive bond material comprises cured ureaformaldehyde resin, in an amount of at least 40% by weight of the total adhesive bond layer, exclusive of any filler.
4. A coated abrasive according to claim 3, characterized by the fact that said outermost layer of adhesive bond material further comprises the residue after curing of a latent curing system consisting essentially of:
 - (1) an ammonium salt of an acid having a disassociation constant of at least 10^{-4} ; and
 - (2) an amino compound having at least one primary amino group attached to a tertiary carbon atom and having a hydroxyl or ether oxygen atom attached to a second carbon atom adjacent said tertiary carbon atom, said amino compound being present in a quantity sufficient to raise the pH of total adhesive composition to a value of from 6 to 9 prior to cure of the adhesive.
5. A coated abrasive according to claim 4, characterized by the fact that said amino compound is 2-methyl-2-aminopropanol, 2-amino-2-methyl-1,3-propanediol, 5-amino-5-methyl-1,3-dioxane, tris(hydroxymethyl)aminomethane, or 2-amino-2-ethyl-1,3-propanediol.
6. A coated abrasive according to any one of the preceding claims, characterized by at least two adhesive layers, where the next to outermost of said layers comprises at least 40% by volume of animal glue or dried latex.

20 Patentansprüche

1. Beschichtetes Schleifmittelprodukt mit einer flexiblen Tragschicht, mit einer Mehrzahl von Schleifkornteilchen, die über mindestens eine Oberfläche der Tragschicht verteilt sind, und mit mindestens einer Schicht aus einem Klebstoffbindemittel, durch das die Schleifkornteilchen miteinander und mit der Tragschicht verklebt sind, dadurch gekennzeichnet, daß die äußerste Schicht aus Klebstoffbindemittel umfaßt:
 - (a) tierischen Leim oder ein gehärtetes Aminoharz oder ein Gemisch derselben in einer Menge von mindestens 40 Gew.% der Gesamtmenge des Klebstoffbindemittels ohne einen gegebenenfalls vorhandenen Füllstoff und
 - (b) in einer Menge von mindestens 0,74 g/m², aber von nicht mehr als 10% des Gesamtgewichtes des in der genannten Außenschicht enthaltenen Klebstoffbindemittels ohne einen gegebenenfalls vorhandenen Füllstoff einen Zusatzstoff, der aus
 - (1) einem Teilester der Phosphorsäure,
 - (2) einem Salz eines Teilesters der Phosphorsäure mit einem Amin,
 - (3) einem Tetraorganylammoniumsalz oder
 - (4) einem löslichen Gemisch derselben besteht.
2. Beschichtetes Schleifmittel nach Anspruch 1, dadurch gekennzeichnet, daß der genannte Zusatzstoff in der äußersten Klebstoffschicht mindestens eine Lange Organylgruppe pro Molekül enthält.
3. Beschichtetes Schleifmittel nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die äußerste Klebstoffschicht gehärtetes Harnstoffformaldehydharz in einer Menge von mindestens 40 Gew.% der Gesamtmenge der Klebstoffbindemittelschicht ohne einen gegebenenfalls vorhandenen Füllstoff enthält.
4. Beschichtetes Schleifmittel nach Anspruch 3, dadurch gekennzeichnet, daß die äußerste Schicht des Klebstoffbindemittels außerdem den Rückstand enthält, der nach dem Härteten eines latenten härtbaren Systems verbleibt, das im wesentlichen besteht aus
 - (1) einem Ammoniumsalz einer Säure mit einer Dissoziationskonstante von mindestens 10^{-4} und
 - (2) einer Aminoverbindung mit mindestens einer an ein tertiäres Kohlenstoffatom angelagerten, primären Aminogruppe und mit einem Hydroxyl- oder Ethersauerstoffatom, das an einem dem genannten tertiären Kohlenstoffatom benachbarten zweiten Kohlenstoffatom angelagert ist, wobei die Aminoverbindung in einer Menge vorhanden ist, die genügt, um den pH-Wert der Gesamt-Klebstoffzusammensetzung vor dem Härteten des Klebstoffes auf einen Wert im Bereich von 6 bis 9 zu erhöhen.
5. Beschichtetes Schleifmittel nach Anspruch 4, dadurch gekennzeichnet, daß die genannte Aminoverbindung 2-Methyl-2-aminopropanol, 2-Amino-2-methyl-1,3-propandiol, 5-Amino-5-methyl-1,3-dioxan, Tris(hydroxymethyl)aminomethan oder 2-Amino-2-ethyl-1,3-propandiol besteht.
6. Beschichtetes Schleifmittel nach einem der vorhergehenden Ansprüche, gekennzeichnet durch mindestens zwei Klebstoffschichten, von denen die zweitäußerste Schicht mindestens 40 Vol.% tierischen Leim oder getrockneten Latex enthält.

60 Revendications

1. Article à revêtement abrasif comprenant un support flexible, une pluralité de particules de grains abrasifs dispersées sur la surface d'au moins une face de ce support, et au moins une couche d'une matière liante adhésive qui fait adhérer les dites particules de grains abrasifs les unes aux autres et au support, caractérisé par le fait que la couche extrême extérieure de la dite matière liante adhésive comprend:

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(a) une colle animale, ou une résine amino durcie, ou un mélange de ces substances, en une quantité d'au moins 40% en poids de la matière liante adhésive totale, à l'exclusion de toute charge; et

(b) au moins 0,74 gramme par mètre carré, mais pas plus de 10% du poids total de la matières liante adhésive totale contenue dans la dite couche extérieure, à l'exclusion de toute charge, d'un additif qui est

5 (1) une ester partiel d'acide phosphorique,
(2) un sel d'un ester partiel d'acide phosphorique avec une amine,
(3) un sel de tétraorganylammonium, ou
(4) un mélange soluble de ces substances.

10 2. Article à revêtement abrasif selon la revendication 1, caractérisé par le fait que le dit additif contenu dans la couche adhésive extrême extérieure comporte au moins un groupe organyle long par molécule.

15 3. Article à revêtement abrasif selon la revendication 1 ou 2, caractérisé par le fait que la couche extrême extérieure de matière liante adhésive comprend une résine urée/formaldéhyde durcie, en une quantité d'au moins 40% en poids de la couche liante adhésive totale, à l'exclusion de toute charge.

4. Article à revêtement abrasif selon la revendication 3, caractérisé par le fait que la couche extrême extérieure de matière liante adhésive comprend en outre le résidu après durcissement d'un système durcissant latent essentiellement composé de:

20 (1) un sel d'ammonium d'un acide ayant une constante de dissociation d'au moins 10^{-4} ; et
(2) un composé amino ayant au moins un groupe amino primaire attaché à un atome de carbone tertiaire et ayant un atome d'oxygène d'hydroxyle ou d'éther fixé à un deuxième atome de carbone adjacent au dit atome de carbone tertiaire, le dit composé amino étant présent en une quantité suffisante pour éléver le pH de la composition adhésive totale à une valeur allant de 6 à 9 avant le durcissement de l'adhésif.

25 5. Article à revêtement abrasif selon la revendication 4, caractérisé par le fait que le dit composé amino est le 2-méthyl-2-aminopropanol, le 2-amino-2-méthyl-1,3-propanediol, le 5-amino-5-méthyl-1,3-dioxane, le tris(hydroxyméthyl)aminométhane ou le 2-amino-2-éthyl-1,3-propane-diol.

6. Article à revêtement abrasif selon l'une quelconque des revendications précédentes, caractérisé par au moins deux couches adhésives, dans lesquelles la couche qui suit la plus extérieure des dites couches comprend au moins 40% en volume d'une colle animale ou de latex séché.

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