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MICROPOROUS INKING COMPOSITIONS

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This invention relates to resinous inking compositions and, more particularly, to microporous inking compositions which contain an elastomeric polymeric binder and which are particularly suitable for use in typewriter ribbons as well as in ribbons, tapes and sheets for high-speed printers, tabulators and optical scanning devices. The invention further relates to the improved pressure-sensitive ink-transfer products which are formed from the microporous inking compositions of the invention and which, upon proper sizing, may be employed as typewriter ribbons and ribbons, tapes and sheets for high-speed printers, tabulators and optical scanning devices, as well as to processes for producing several of such products.

In theory, when a microporous inking composition is coated on polymer film as a non-stenciling ink layer, is should be capable of giving repeated impressions without any apparent diminution in the quality or appearance of the image, since the micropores in the polymeric binder should function as a reservoir for the inking compound or formulation. As a general rule, however, resinous inking compositions in which the inking compound is dispersed throughout a polymeric binder do not possess adequate microporosity to hold a sufficient reservoir of inking compound. Polymer films coated with such resinous inking compositions may be used for only one or two impressions before the images begin to fade. Moreover, when an attempt is made to incorporate more inking compound in the resinous binder by using a conventional microporous polymer system (which is one in which the average pore size ranges between 4 and 10 microns), a larger quantity of ink may be incorporated into the resinous inking composition, but any typewriter ribbons formed from such compositions are generally subject to uncontrollable "bleeding" upon typing, resulting in poorly defined images or impressions.

Using an elastomeric polymeric binder which contains a finely ground microporous inorganic filler, such as activated carbon, activated silica, activated alumina, activated calcium silicates and activated clays, all of which fillers are characterized by extremely fine micropores, we have found that it is possible to produce a microporous inking composition by the incorporation of inking compound (which, by itself, is merely an inking pigment dissolved or dispersed in a non-aqueous, non-volatile ink carrier). By incorporating both the finely ground microporous (or "activated," the terms being used interchangeably) inorganic filler and the inking compound in an elastomeric polymeric binder, a large quantity of ink is held in the micropores of the activated inorganic filler and does not rub off until the composition is compressed. Typewriter ribbons and tapes or sheets for high-speed printers which are manufactured from the improved microporous inking compositions of the invention possess an ink-transfer (or ink-releasing, the terms being used interchangeably) capacity far in excess of any presently commercially available typewriter ribbons and high-speed printer tapes and sheets manufactured from resinous inking compositions. In fact, our experience has indicated that the extremely high ink capacity of the activated inorganic filler in the microporous inking compositions of the invention make it possible to obtain at least 25 and in some instances up to 50 excellent impressions without any fading of the image. As used herein, the phrase

"typewriter and high-speed printer ribbons, tapes and sheets" also includes ribbons, tapes and sheets used in other printers, such as tabulators and optical scanning devices.

Based on these discoveries, the invention provides an improved microporous inking composition which is particularly suitable for typewriter and high-speed printer ribbons, tapes and sheets and which comprises a uniformly blended mixture of (i) an elastomeric polymeric binder, (ii) an inking compound comprising a non-aqueous, non-volatile ink carrier containing a high concentration of an ink pigment, and (iii) a finely ground microporous inorganic filler selected from the group consisting of activated carbon, activated silica, activated alumina, activated calcium silicates, and activated clays. The invention further provides improved pressure-sensitive ink-transfer products which are formed from these microporous inking compositions and which, upon proper sizing, may be used as typewriter and high-speed printer ribbons, tapes and sheets.

Selection of a suitable elastomeric polymeric binder for inclusion in the microporous inking compositions of the invention may be made from any film-forming elastomeric polymer (or plasticized polymer) which possesses sufficient strength and durability. Among the many elastomeric polymers which may be used as a resinous binder are the polyalkylenes, such as the atactic and isotactic polymers and interpolymers of ethylene, propylene and butylene, and butadiene; polymers and interpolymers of ethylenic unsaturated compounds, such as styrene, vinyl chloride, vinyl acetate, vinyl fluoride, methacrylic and acrylic acids and their esters, acrylonitrile and dienes (such as the ABS resins); and polyamides produced by the polmerization of diamines and dicarboxylic acids or of aminocarboxylic acids or their lactams. Particularly satisfactory results have been obtained by using polyurethanes (prepared from either polyethers or polyesters or both) as the elastomeric polymeric binder for the microporous inking compositions of the invention. Perhaps the best elastomeric polyurethane binder for this purpose has been found to be the polyester-derived polyurethane elastomer designated as Estane 5740X1, manufactured by B. F. Goodrich Chemical Company, which is characterized by a hardness of 88 Shore A, a tensile strength of 5800 p.s.i., an elongation of 540%, a tensile modulus of 1400 p.s.i. at 300%, a compression set of 39% at 25° C. (22 hours), and a specific gravity of 1.2.

The inking compound employed in the microporous inking compositions of the invention consist essentially of ink pigments, such as soluble dyes, toners, and carbon black, dispersed or dissolved in high concentration in a non-aqueous, non-volatile ink carrier, such as mineral oils. Other components of the ink may be blown oils, heat-bodied oils, dryers, organic solvents or thinners, natural and synthetic resins, and wax-like compounds to modify the tackiness of the particular ink. Typical of such inking compounds is the typewriter ribbon ink which is manufactured by Remington-Rand Division of Sperry-Rand Corporation and sold under the designation XW-144. In general, these inking compounds consist essentially of about 40 parts by weight of extra heavy mineral oil, about 40 parts by weight of wax (such as carnauba wax), and the balance pigment (such as carbon black). It is important, however, that the non-aqueous, non-volatile ink carrier be substantially insoluble in the elastomeric polymeric binder employed in the microporous inking composition. Although a wide range of concentrations of the inking compound may be employed in formulating the microporous inking composition, particularly satisfactory results have been obtained by using from about 100 percent to about 400 percent by weight

of the inking compound based on the weight of the elastomeric polymeric binder contained in the microporous inking composition.

The third essential component in the microporous inking composition of the invention is the finely ground microporous inorganic filler which contains very small micropores (below about 4 microns and preferably below about 1 micron) and which increases the ink-carrying capacity of the microporous inking composition. Although finely ground activated carbon (such as Type JF–6 Activated Carbon manufactured by Barnebey-Cheney Company or Nuchar A manufactured by West Virginia Pulp & Paper Company) has been found to be the most desirable microporous inorganic filler of those tested, excellent results may also be obtained by using activated silica (such as Cab-O-Sil manufactured by Cabot Corporation), activated alumina, activated calcium silicates (such as Microcel manufactured by Johns-Manville Company), diatomaceous earths and other activated clays (such as Dicalite manufactured by Great Lakes Carbon Company), and other natural and synthetic compounds which possess comparable microporous structures. By definition, the total surface area of activated carbon ranges between 2×10^4 and 6×10^4 sq. cm. per gram. The amount of the finely ground microporous inorganic filler incorporated in the microporous inking composition depends, to a large extent, on the concentration and type of inking compound which is to be employed, but in general concentrations of from about 10 percent to about 200 percent by weight may be used, based on the weight of the elastomeric polymeric compound contained in the microporous inking composition.

The three components of the microporous inking composition, namely (i) the elastomeric polymeric binder, (ii) the inking compound which consists essentially of a non-aqueous, non-volatile ink carrier containing an inking pigment, and (iii) the finely ground microporous inorganic filler, may be milled until the composition has reached the proper viscosity, or may be dispersed in a volatile solvent which is capable of dissolving both the ink carrier and the elastomeric polymeric binder, and thereafter employed in the form of a dispersion. Alternatively, both plastisol and organosol techniques may be employed to formulate the microporous inking composition and use it in the production of the pressure-sensitive ink-transfer products of the invention. When a volatile solvent is used, however, in formulating the microporous inking composition, the best results are obtained when the solvent is used in concentrations in the range from about 200 percent to about 600 percent by weight, based on the weight of the elastomeric polymeric binder contained or used in the microporous inking composition.

In general, there are three types of pressure-sensitive ink-transfer products which may be formed from the microporous inking compositions of the invention and which, upon proper sizing, may be used as typewriter and high-speed printer ribbons, tapes and sheets. Broadly, these three types of products include, firstly, unsupported films of the microporous inking composition, in which the composition is processed into a film of sufficient strength; secondly, fiber-reinforced films of the microporous inking composition, in which either natural or synthetic fibers (either woven or non-woven) are used to reinforce a film of the microporous inking composition or, alternatively, the composition is thoroughly impregnated into a woven ribbon or into a ribbon or tape cut from broad woven piece goods of such fibers; and thirdly, supported films of the microporous inking compositions, in which a preformed polymer film is coated over substantially its entire working surface with an inking layer (or film) of the microporous inking composition. Upon proper sizing, any one of these three types of pressure-sensitive ink-transfer products may be used as typewriter ribbons or as high-speed printer tapes or sheets.

Unsupported films of the microporous inking composition may be formed by casting a dispersion in a volatile organic solvent of the microporous inking composition; evaporation of the solvent will usually result in a suitable film. Alternatively, a plastisol or organosol containing the essential components of the microporous inking composition may be fused into an unsupported film which, because it contains the three essential components of the microporous inking composition of the invention (elastomeric polymeric binder, inking compound, and finely ground microporous inorganic filler), will release ink upon compression of the film.

Fiber-reinforced films of the microporous inking composition of the invention may be formed by coating or impregnating a woven or non-woven fabric of either natural or synthetic fibers with a dispersion in a volatile solvent of the microporous inking composition so that evaporation of the solvent will leave a thin film of coating on the fabric. Alternatively, the fabric may be coated or impregnated with a plastisol or organosol containing the three essential components of the microporous inking composition so that upon heating, the particular plastisol or organosol will fuse to a thin film of coating on the fabric. In both cases, the adhesion of the inking film to the fabric may be increased by applying the microporous inking composition to either a woven or non-woven fabric which has previously been impregnated (or treated) with an elastomeric polymer, preferably of the same or similar chemical structure as the elastomeric polymeric binder employed in the microporous inking composition.

Fiber-reinforced films of the microporous inking composition are particularly effective where distortion of the product must be minimized, as in tapes and sheets for high-speed printers. For example, when a polyurethane-impregnated non-woven fabric (which is prevented from elongating out of shape by the fibers) of synthetic fibers is further impregnated with a microporous inking composition containing an elastomeric polyurethane binder, the resultant pressure-sensitive ink-transfer product posesses excellent adhesion between the fabric and the inking film of microporous inking composition. The fibers aid in preventing cutting when the product is used in high-speed printers, while the polyurethane provides a smooth film and the proper resiliency. Any type of fabric may be used in either of the aforementioned techniques, the selection of an appropriate fabric or type of fiber being dependent upon availability and cost.

Supported films of the microprous inking compositions of the invention may be formed by casting a dispersion in a volatile solvent of the microporous inking composition over substantially the entire working surface of a preformed polymer film which functions as a base layer. Depending upon the particular preformed polymer film which is used as the base layer and the chemical composition of the elastomeric polymeric binder contained in the microporous inking composition, the preformed polymer film may require appropriate surface treatment (or "frosting") to insure bonding of the microporous inking composition to its working surface. Evaporation of the solvent will then leave an inking layer bonded to the base layer over substantially its entire working surface and comprising a substantially continuous film of the microporous inking composition.

Apart from strength and resiliency, there is nothing particularly critical about the selection of a suitable preformed polymer film as the base layer in producing the third type of pressure-sensitive ink-transfer products in accordance with the invention. Among the most satisfactory polymer films for this purpose is polyethylene terephthalate (such as Mylar manufactured by E. I. du Pont de Nemours and Company), although other polymer films may be employed, including those films formed

from isotactic polyethylene and polypropylene to cite but a few. The thickness of the base layer may vary, of course, but in general polymer films of from 0.2 to 2 mils may be used, depending upon the desired strength.

The following examples are illustrative of the ease with which the improved microporous inking compositions and the pressure-sensitive ink-transfer products of the invention may be produced:

Example I

A microporous inking composition was prepared by uniformly blending 100 parts by weight of an elastomeric polyurethane binder (Estane 5740X1 manufactured by B. F. Goodrich Chemical Company), 50 parts by weight of finely ground activated carbon (JF–6 Activated Carbon manufactured by Barnebey-Cheney Company), and 200 parts by weight of ink (XW–144 manufactured by Remington-Rand Division of Sperry-Rand Corporation) in 150 parts by weight of tetrahydrofuran and 150 parts by weight of dimethyl formamide.

The resultant dispersion was then coated over a nonwoven fabric of synthetic fabric previously impregnated with an elastomeric polyurethane (Estane 5740X1) and over a preformed film of "frosted" polyethylene terephthalate; evaporation of the solvents (tetrahydrofuran and dimethyl formamide) yield a fiber-reinforced film of the microporous inking composition in the first case, and a supported film in the second case, both of which products, upon proper sizing, were particularly satisfactory for use as typewriter ribbons, giving at least 25 excellent impressions before there was any noticeable fading in the appearance of the image. Interestingly, ribbons of the fiber-reinforced film possessed from three to four times the life of the supported film under identical typing conditions.

Example II

Using a solvent system of 150 parts by weight of tetrahydrofuran and 150 parts by weight of dimethyl formamide, a microporous inking composition was prepared by adding to such solvent system 100 parts by weight of an elastomeric polyurethane binder (Estane 5740X1), 100 parts by weight of activated carbon (JF–6 Activated Carbon), and 266 parts by weight of ink (XW–144).

The resultant dispersion could be used to prepare unsupported and supported films as well as fiber-reinforced films by the aforementioned techniques.

Example III

A dispersion of a microporous inking composition was prepared with the following formulation:

	Parts
Polyurethane (Estane 5740X1)	100
Activated carbon (JF–6)	150
Ink (XW–144)	333
Tetrahydrofuran	150
Dimethyl formamide	150

This formulation could also be used to prepare the three types of pressure-sensitive ink-transfer products described previously.

Example IV

A dispersion of a microporous inking composition was prepared by uniformly blending 100 parts by weight of an elastomeric polyurethane binder (Estane 5740X1), 25 parts by weight of activated carbon (Nuchar A manufactured by West Virginia Pulp & Paper Company), and 133 parts by weight of ink (XW–144) in 150 parts by weight of tetrahydrofuran and 150 parts by weight of dimethyl formamide.

As before, this formulation could be employed to produce both supported and unsupported films as well as fiber-reinforced films by the aforementioned techniques, each of which pressure-sensitive ink-transfer products may be used as typewriter and high-speed printer ribbons, tapes and sheets.

Although the foregoing examples demonstrate the advantage of preparing the microporous inking compositions and the pressure-sensitive ink-transfer products of the invention with elastomeric polyurethane binders and activated carbon, similar results may be obtained by using any elastomeric polymeric binder together with any finely ground microporous inorganic filler.

We claim:

1. A microporous inking composition suitable for use in typewriter and high-speed printer ribbons, tapes and sheets consisting essentially of a uniformly blended mixture of (i) an elastomeric polyurethane binder selected from the group consisting of polyester-derived and polyether-derived elastomeric polyurethane binders, (ii) from about 100 percent to about 400 percent by weight of an inking compound consisting essentially of a wax-modified mineral oil ink carrier which is substantially insoluble in the elastomeric polyurethane binder and which contains a high concentration of an ink pigment, and (iii) from about 10 percent to about 200 percent by weight of a finely ground, microporous activated carbon, all percentages being based upon the weight of the elastomeric polyurethane binder contained in the microporous inking composition, the ink pigment and the finely ground microporous activated carbon being different substances.

2. A pressure-sensitive ink-transfer product suitable for use in typewriter and high-speed printer ribbons, tapes and sheets comprising an unsupported film of a microporous inking composition consisting essentially of a uniformly blended mixture of (i) an elastomeric polyurethane binder selected from the group consisting of polyester-derived and polyether-derived elastomeric polyurethane binders, (ii) from about 100 percent to about 400 percent by weight of an inking compound consisting essentially of a wax-modified mineral oil ink carrier which is substantially insoluble in the elastomeric polyurethane binder and which contains a high concentration of an ink pigment, and (iii) from about 10 percent to about 200 percent by weight of a finely ground microporous activated carbon, all percentages being based upon the weight of the elastomeric polyurethane binder contained in the microporous inking composition, the ink pigment and the finely ground microporous activated carbon being different substances.

3. A pressure-sensitive ink-transfer product suitable for use in typewriter and high-speed printer ribbons, tapes and sheets comprising (a) a base layer of a polymer film; and (b) an inking layer bonded to the base layer of polymer film over substantially its entire working surface and comprising a substantially continuous film of a microporous inking composition consisting essentially of uniformly blended mixture of (i) an elastomeric polyurethane binder selected from the group consisting of polyester-derived and polyether-derived elastomeric polyurethane binders, (ii) from about 100 percent to about 400 percent by weight of an inking compound consisting essentially of a wax-modified mineral oil ink carrier which is substantially insoluble in the elastomeric polyurethane binder and which contains a high concentration of an ink pigment, and (iii) from about 10 percent to about 200 percent by weight of a finely ground microporous activated carbon, all percentages being based upon the weight of the elastomeric polyurethane binder contained in the microporous inking composition, the ink pigment and the finely ground microporous activated carbon being different substances.

4. A pressure-sensitive ink-transfer product suitable for use in typewriter and high-speed printer ribbons, tapes and sheets comprising (a) a base layer of polyethylene terephthalate film; and (b) an inking layer bonded to the base layer of polyethylene terephthalate film over substantially its entire working surface and comprising a substantially continuous film of a microporous inking composition consisting essentially of a uniformly blended mixture of (i) an elastomeric polyurethane binder selected from the group consisting of polyester-de-

rived and polyether-derived elastomeric polyurethane binders, (ii) from about 100 percent to about 400 percent by weight of an inking compound consisting essentially of a wax-modified mineral oil ink carrier which is substantially insoluble in the elastomeric polyurethane binder and which contains a high concentration of an ink pigment, and (iii) from about 10 percent to about 200 percent by weight of a finely ground microporous activated carbon, all percentages being based upon the weight of the elastomeric polyurethane binder contained in the microporous inking composition, the ink pigment and the finely ground microporous activated carbon being different substances.

5. A pressure-sensitive ink-transfer product suitable for use in typewriter and high-speed printer ribbons, tapes and sheets comprising a fiber-reinforced film of a microporous inking composition consisting essentially of a uniformly blended mixture of (i) an elastomeric polyurethane binder selected from the group consisting of polyester-derived and polyether-derived elastomeric polyurethane binders, (ii) from about 100 percent to about 400 percent by weight of an inking compound consisting essentially of a wax-modified mineral oil ink carrier which is substantially insoluble in the elastomeric polyurethane binder and which contains a high concentration of an ink pigment, and (iii) from about 10 percent to about 200 percent by weight of a finely ground microporous activated carbon, all percentages being based upon the weight of the elastomeric polyurethane binder contained in the microporous inking composition, the ink pigment and the finely ground microporous activated carbon being different substances.

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