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MICROPOROUS TYPEWRITER RIBBONS

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This application is a continuation-in-part of our copending application Ser. No. 330,611, filed Dec. 16, 1963, entitled "Microporous Inking Compositions," now United States Letters Patent No. 3,330,791.

This invention relates to typewriter and high-speed printer ribbons, tapes and sheets which contain a microporous inking composition and which, consequently, may be collectively designated as "microporous typewriter ribbons." The invention provides new and improved pressure-sensitive ink-transfer products which contain a unique microporous inking composition and which, upon proper sizing, may be employed as typewriter ribbons as well as ribbons, tapes and sheets for high-speed printers, tabulators and optical scanning devices.

In theory, when a microporous inking composition is coated on polymer film as a non-stenciling ink layer, it 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 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.

These difficulties may be obviated by using the unique microporous inking compositions described in our copending application Ser. No. 330,611, now United States Letters Patent No. 3,330,791, the essential components of which microporous inking composition are (i) an elastomeric polymeric binder, (ii) an inking compound which, by itself, is merely an inking pigment dissolved or dispersed in a non-aqueous, non-volatile ink carrier, and (iii) a finely ground microporous (or "activated," the terms being used interchangeably) inorganic filler. Typewriter ribbons and tapes or sheets for high-speed printers which have been manufactured from these unique microporous inking compositions possess an ink-transfer (or ink-releasing, both 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. Indeed, experience has indicated that the extremely high ink capacity of the activated inorganic filler in these unique microporous inking compositions make it possible to obtain at least 25 and, in some instances, up to 50 excellent impressions without any fading of the image.

The present invention is based upon the discovery that when the degree of resiliency of a typewriter ribbon which contains the aforementioned microporous inking composition is increased in a direction normal (or perpendicular) to the plane of such typewriter ribbon, it is possible to

significantly increase the durability of the ribbon and to improve its print quality. By fabricating the typewriter ribbon from a shock-absorbent base layer of an elastomeric polymer film having a high degree of resiliency in a direction normal to the plane of such film, the function of which base layer is to cushion the impact of the typewriter key when it strikes the ribbon, the durability of the ribbon is greatly improved (and consequently its useful life is extended) and, more importantly, the print quality or image sharpness of the ribbon actually improves, probably because the elastomeric properties of these ribbons enable them to "wrap around" the typeface of the typewriter key more tautly than typewriter ribbons which are not as resilient.

Using this structure, two types of pressure-sensitive, ink-transfer products suitable for use in typewriter and high-speed printer ribbons, tapes and sheets have been formed. Broadly, these two types of products include, firstly, those products in which an unsupported, shock-absorbent base layer of an elastomeric polymer film is coated over substantially its entire working surface with a film or layer of the microporous inking composition, and secondly, those products in which a shock-absorbent base layer is applied to the back (or exposed face) of a thin, non-elastic polymer film, the working surface of which is coated with a film or layer of the microporous inking composition. 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 pressure-sensitive, ink-transfer product suitable for use in typewriter and high-speed printer ribbons, tapes and sheets which comprises (a) a shock-absorbent base layer of an elastomeric polymer film having a high degree of resiliency in a direction normal to the plane of such film, and (b) an inking layer bonded to the shock-absorbent base layer of elastomeric polymer film over substantially its entire working surface and comprising a substantially continuous film of a microporous inking composition which, in turn, 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. Alternatively, the structure of the pressure-sensitive, ink-transfer product of the invention may comprise (a) a shock-absorbent base layer of an elastomeric polymer film having a high degree of resiliency in a direction normal to the plane of such film, (b) an intermediate layer of a thin, non-elastic polymer film bonded to the shock-absorbent base layer, and (c) an inking layer bonded to the intermediate layer and comprising a substantially continuous film of the microporous inking composition.

Selection of a suitable elastomeric polymeric binder for inclusion in the microporous inking compositions used in accordance with 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 polymerization 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.

The inking compound employed in these microporous inking compositions 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. 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 these microporous inking compositions 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. 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.

To prepare the first type of pressure-sensitive, ink-transfer product in accordance with the invention, a dispersion in a volatile solvent of the microporous inking composition is cast or coated over substantially the entire working surface of a preformed elastomeric polymer film which functions as a shock-absorbent base layer and which possesses a high degree of resiliency in a direction normal to the plane of the film. Depending upon the particular preformed elastomeric polymer film which is used as the shock-absorbent base layer and the composition of the elastomeric polymeric binder contained in the microporous inking composition, the preformed elastomeric 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 shock-absorbent base layer over substantially its entire working surface and comprising a substantially continuous film of the microporous inking composition. Because the composite product has elastomeric properties, this type of pressure-sensitive, ink-transfer product may be formed, after suitable sizing, into "all-elastic" typewriter and high-speed printer ribbons, tapes and sheets which are characterized by higher durability and better print quality than fabric typewriter ribbons or non-elastic typewriter ribbons.

The second type of pressure-sensitive, ink-transfer product of the invention is usually prepared by applying a film or layer of the elastomeric polymer, which functions as a shock-absorbent base layer, to the back of a thin, non-elastic polymer film on the opposite (or working) face of which is a layer of the microporous inking composition. Because this thin film of non-elastic polymer is now coated on both sides, one side being coated with the inking layer and the other side being coated with the shock-absorbent base layer, it now becomes an "intermediate" layer. Structurally, this product comprises (a) a shock-absorbent base layer of an elastomeric polymer film having a high degree of resiliency in a direction normal to the plane of such film, (b) an intermediate layer of a thin, non-elastic polymer film bonded to the shock-absorbent base layer, and (c) an inking layer bonded to the intermediate layer over substantially its entire working face with a substantially continuous film of the microporous inking composition.

Selection of a suitable elastomer polymer for forming the shock-absorbent base layer for both types of pressure-sensitive, ink-transfer products may be made from any elastomeric polymer which is capable of being cast or blown into a film having a high degree of resiliency (i.e., approaching 100 percent) in a direction normal to the plane of such film. Suitable elastomeric polymers for fabricating the shock-absorbent base layer include elastomeric polyurethanes (either polyester- or polyether-derived, or both), natural rubber, neoprene, and elastomeric ethylene-propylene interpolymers to cite but a few. Substantial improvements in the durability of both types of pressure-sensitive, ink-transfer products may be made by embossing a pattern on the exposed face of the shock-absorbent base layer.

Apart from strength and resiliency, there is nothing particularly critical about the selection of a suitable preformed polymer film as the intermediate layer in producing the second 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 & Company), although other non-elastic polymer films may be employed, including those films formed from isotactic polyethylene and polypropylene to cite but a few. The thickness of the intermediate 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 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 preformed film of an elastomeric polyurethane (Estane 5740X100); evaporation of the solvents (tetrahydrofuran and dimethyl formamide) left a substantially continuous film of the microporous inking composition bonded over substantially the entire working surface ofthe polyurethane base layer. Upon proper sizing, the product was formed into typewriter ribbons. Testing of these elastic typewriter ribbons in electric typewriters under a variety of operating conditions demonstrated that these ribbons were more flexible, more durable and possessed better print quality than any other typewriter ribbon presently commercially available. By embossing a criss-cross pattern onto the exposed face of the shock-absorbent base layer of elastomeric polyurethane, it was possible to improve the durability of the product even further.

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 the two types of pressure-sensitive, ink-transfer products of the invention by the aforementioned techniques.

EXAMPLE III

A dispersion of the 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 two 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 types of pressure-sensitive, ink-transfer products of the invention 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 demonstrates 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 pressure-sensitive, ink-transfer product suitable for use in typewriter and high-speed printer ribbons, tapes and sheets comprising (a) a shock-absorbent base layer of an elastomeric polymer film having a high degree of resiliency in a direction normal to the plane of such film; (b) an intermediate layer of a thin, non-elastic polymer film bonded to the shock-absorbent base layer; and (c) an inking layer bonded to the intermediate layer of non-elastic polymer 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 polymeric binder, (ii) an inking compound comprising a non-aqueous, non-voltatile ink carrier which is substantially insoluble in the elastomeric polymeric binder and which contains a high concentration of an ink pigment, and (iii) a finely ground microporous inorganic filler.

2. A pressure-sensitive, ink-transfer product suitable for use in typewriter and high-speed printer ribbons, tapes and sheets comprising (a) a shock-absorbent base layer of an elastomeric polymer film having a high degree of resiliency in a direction normal to the plane of such film; (b) an intermediate layer of a thin, non-elastic polymer film bonded to the shock-absorbent base layer; and (c) an inking layer bonded to the intermediate layer of non-elastic polymer film over substantially its entire working surface and comprising a substantially continuous film of a microporus inking composition consisting essentially of a uniformly blended mixture of (i) an elastomeric polymeric binder, (ii) an inking compound comprising a non-aqueous, non-volatile ink carrier which is substantially insoluble in the elastomeric polymeric binder and which contains 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.

3. A pressure-sensitive, ink-transfer product suitable for use in typewriter and high-speed printer ribbons, tapes and sheets comprising (a) a shock-absorbent base layer of an elastomeric polymer film having a high degree of resiliency in a direction normal to the plane of such film; (b) an intermediate layer of a thin, non-elastic polymer film bonded to the shock-absorbent base layer; and (c) an inking layer bonded to the intermediate layer 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, (ii) from about 100 percent to about 400 percent by weight of an inking compound comprising a non-aqueous, non-volatile 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 microporus inorganic filler selected from the group consisting of activated carbon, activated silica, activated alumina, activated calcium silicates, and activated clays, all percentages being based upon the weight of the elastomeric polyurethan binder contained in the microporous inking composition.

4. A pressure-sensitive, ink-transfer product suitable for use in typewriter and high-speed printer ribbons, tapes and sheets comprising (a) a shock-absorbent base layer of an elastomeric polyurethane film having a high degree of resiliency in a direction normal to the plane of such film; (b) an intermediate layer of a thin, nonelastic polymer film bonded to the shock-absorbent base layer; and (c) an inking layer bonded to the intermediate layer 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, (ii)

from about 100 percent to about 400 percent by weight of an inking compound comprising a non-aqueous, non-volatile 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.

5. A pressure-sensitive, ink-transfer product suitable for use in typewriter and high-speed printer ribbons, tapes and sheets comprising (a) a shock-absorbent base layer of an elastomeric polyurethane film having a high degree of resiliency in a direction normal to the plane of such film; (b) an intermediate layer of a thin, non-elastic polyethylene terephthalate film bonded to the shock-absorbent base layer; and (c) an inking layer bonded to the intermediate layer 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, (ii) from about 100 percent to about 400 percent by weight of an inking compound comprising a non-aqueous, non-volatile 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.

6. A pressure-sensitive, ink-transfer product suitable for use in typewriter and high-speed printer ribbons, tapes and sheets comprising (a) a shock-absorbent base layer of an elastomeric polyurethane film having a high degree of resiliency in a direction normal to the plane of such film; (b) an intermediate layer of a thin, non-elastic polymer film bonded to the shock-absorbent base layer; and (c) an inking layer bonded to the intermediate layer 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, (ii) from about 100 percent to about 400 percent by weight of an inking compound comprising a non-aqueous, non-volatile 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 inorganic filler selected from the group consisting of activated carbon, activated silica, activated alumina, activated calcium silicates, and activated clays, all percentages being based upon the weight of the elastomeric polyurethane binder contained in the microporous inking composition, the exposed face of the shock-absorbent base layer of elastomeric polyurethane film containing an embossed pattern to improve the durability of the shock-absorbent base layer.

7. A pressure-sensitive, ink-transfer product suitable for use in typewriter and high-speed printer ribbons, tapes and sheets comprising (a) a shock-absorbent base layer of an elastomeric polyurethane film having a high degree of resiliency in a direction normal to the plane of such film; (b) an intermediate layer of a thin, non-elastic polyethylene terephthalate film bonded to the shock-absorbent base layer; and (c) an inking layer bonded to the intermediate layer 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, (ii) from about 100 percent to about 400 percent by weight of an inking compound comprising a non-aqueous, non-volatile 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 exposed face of the shock-absorbent base layer of elastomeric polyurethane film containing an embossed pattern to improve the durability of the shock-absorbent base layer.

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