

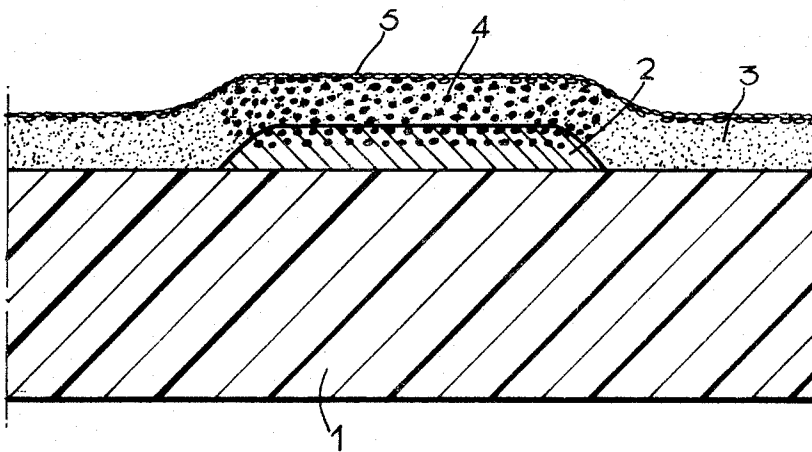
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PROCESS FOR MAKING A DRY TRANSFER MATERIAL

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PROCESS FOR MAKING A DRY TRANSFER MATERIAL

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4 Claims

ABSTRACT OF THE DISCLOSURE

In a dry transfer material comprising a support, ink signs and a pressure-sensitive adhesive layer covering both the ink signs and the parts of the support without ink signs, the adhesive layer has on its free surface a layer of fine solid particles such that the adhesive cannot act unless a sufficient pressure is applied during a sufficient period of time to allow the adhesive to pass through the particle layer and to cause the ink signs to be transferred to adhere to a receptor surface. The ink signs contain a non-volatile liquid material capable of oozing into the adhesive layer so as to reduce the viscosity of the latter.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The present invention relates to a dry transfer material i.e. a material for effecting under dry conditions the transfer of one or more ink signs or indicia from a support carrying the same to a receptor surface. It also relates to a process for making such a dry transfer material.

The term "ink signs" as used herein is intended to mean any figure or part of figure, for example, drawing, letter, numeral, punctuation mark printed or applied in any other way onto a support.

(2) Description of the prior art

Known transfer assemblies of the kind described comprise a sheet supporting said ink signs as well as a pressure-sensitive adhesive layer covering both the ink signs and the portions of the supporting sheet without signs.

Thus, the prior art discloses dry transfer material for making dry decalcomania pictures with transfer materials comprising very tacky adhesives, similar to those used in the adhesive tape industry.

These transfer materials offer the advantage of providing very good adhesions between the ink sign and the receptor surface. However, the strong superficial adhesion effect of these adhesives does not allow the ink sign to slide and to be properly positioned on the receptor surface. Moreover, the ink sign can always be undesirably removed from the supporting sheet.

Dry transfer assemblies are also known wherein the adhesive has a slight tacky touch. These types of adhesives generally are made of waxes or waxy materials mixed with pressure-sensitive adhesives which allow the ink signs to slide on the receptor surface and to be adjusted thereon. However, their adhesive power is reduced by the waxy materials.

SUMMARY OF THE INVENTION

The present invention has for its object a dry transfer material having the advantages of the known systems without the drawbacks of the latter. In other words, the ink signs should be easily slidable and adjustable on the receptor sheet without any reduction of property such as the adhesive power of the pressure-sensitive adhesive.

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For this purpose, in a dry transfer material according to this invention, the free surface of the adhesive layer has a layer of solid particles joined side by side to one another, in such a way that the free surface of the adhesive layer substantially has no adhesiveness, said particles having a maximum size of 50 millimicrons, a specific gravity below 3 and a refractive index below 1.7, whereby the adhesive cannot pass through said layer of particles, wet the latter and reach the receptor surface unless a sufficient pressure is applied onto the face of the supporting sheet opposed to that face which carries the signs and the adhesive layer, and the ink signs contain a non volatile liquid material capable of oozing into the adhesive layer so as to reduce the viscosity of the latter and to facilitate the dispersion of said particles in the adhesive layer when said pressure is applied.

This invention also relates to a process for making a dry transfer material for dry transferring ink signs to a receptor surface, in which process ink signs and a pressure-sensitive adhesive layer are successively applied onto a supporting sheet. According to the present invention, an adhesive is used which comprises a volatile fraction and a non volatile fraction and contains solid particles of a maximum size of 50 millimicrons, a specific gravity below 3 and a refractive index below 1.7, the said solid particles being dragged towards the free surface of the adhesive layer under the action of the volatile fraction during the evaporation of the latter so as to form a layer of solid nontacky particles joined side by side to one another at said surface, and with the ink of said signs, a liquid non volatile material is incorporated, said material being capable of oozing into the adhesive layer so as to reduce the viscosity of the latter.

DETAILED DESCRIPTION OF THE INVENTION

Hereinafter some further details are given concerning the various components of this invention.

According to the present invention, the supporting sheet comprises, at least at the surface thereof carrying the ink signs, a hydrocarbon polymer such as polyethylene or polystyrene having a critical surface tension below 37 dynes/cm. After application of the ink signs and before application of the adhesive layer, the polarity of the surface of the supporting sheet is modified in order to enhance the bonding between the adhesive layer and the supporting sheet at the places thereof where said surface does not carry any ink signs, while taking care not to reinforce the weak adhesion between the ink and the support and not to destroy the ink. This modification may be carried into effect by bombarding the said surface by means of ions for obtaining the conditions needed for a good adhesion.

For this purpose, a supporting sheet is passed through an apparatus which modifies the surface polarity thereof by ion bombarding the same in high voltage alternating electric fields, an apparatus of the EL-type, available from the German firm DEMES, may be used therefor.

Since only the surface of the provisional support which receives the ink signs is of importance, either self-sustaining hydrocarbon polymer films or transparent paper sheets covered with a layer of hydrocarbon polymer may be used. The use of supports made of transparent paper is advisable when the thin films of hydrocarbon polymers do not have sufficient rigidity for meeting the requirements of printing processes.

A good spreading or coating of ink is obtained on said supports as well as a weak adhesion allowing the ink film to be well separated or stripped as a result of the tractive force of the pressure-sensitive adhesive by using inks or varnishes whose surface layer is formed by evaporation.

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poration of the solvents and whose binder comprises linear thermoplastic resins. For example, polyvinyl butyral, nitrocellulose, ethylcellulose are quite suitable. These resins are normally plastified according to the known principles for imparting to the dry ink film good resilient characteristics.

The ink contains in addition, according to the present invention, a non volatile liquid material adapted for oozing into the adhesive layer which will cover the ink sign, so as to lower the viscosity thereof. This liquid non volatile material preferably has a molecular weight below 600. It should be inert with regard to the polymer of the ink and incapable of forming solvates therewith so that it may easily ooze out of the molecular chains. Examples of oozing non volatile materials include di(2-ethylhexyl) azelate, butyl stearate, triethyl phosphate, vegetable and mineral oils.

When the ink sign is made of several superimposed layers of different colours, it is not necessary to incorporate the exuding material or fluidity agent with all layers. Only the last layer in contact with the adhesive should contain said exuding material. The last layer, or the sole layer when the ink sign only comprises one layer, preferably has a thickness of at least 7 microns.

In an advantageous embodiment of the present invention, the fluidity agent in the form of an exuding material also is a plasticizer with respect to the pressure-sensitive adhesive which improves the adhesion properties of the adhesive. Thus, butyl stearate and ricinus oil (castor oil) are plasticizers of polyvinylethylether.

For example, the following ink formulae may be used according to the present invention.

Ink Formula 1:	Parts by weight
Nitrocellulose ½ second	100
Rosin ester	10
Diocetyl phtalate	40
Butyl alcohol	50
Isopropylglycol	344
Ethylglycol acetate	208
Butyl stearate	12
Ricinus oil (castor oil)	5

Ink Formula 2:	Parts by weight
Polyvinyl butyral	100
Diocetyl phtalate	8
Isopropyl alcohol	60
Butylglycol	40
Di(2-ethylhexyl) azelate	10

These formulae give transparent ink films. In order to obtain coloured films, one adds the necessary pigments thereto.

Pressure-sensitive adhesives have been known for a long time. They comprise a cohesion agent which may be a natural or synthetic elastomer or a high molecular weight polymer, and a thermoplastic compatible material giving adhesion and adhesive power, which may be a tacky resin or a low molecular weight polymer.

Such adhesives ordinarily used in the manufacture of adhesive tapes have a tractive power greater than the adhesion power of the ink on the provisional support. They give a very good adhesion of ink on the receptor surface and may be used according to the present invention. Examples of adhesive formulae are given hereinafter.

Adhesive Formula 1:	Parts by weight
Polyvinylethylether, molecular weight above 100,000, cohesion agent	40
Polyvinylethylether, molecular weight below 30,000, adhesion agent	60
Toluene	10
Benzine 100/140, aliphatic solvent	200
Heptane	90

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Adhesive Formula 2:	Parts by weight
Latex crepe-rubber, cohesion agent	50
Styrene-butadiene rubber (S.B.R.) cohesion agent	50
Alkyl polyhydroxyphenol, antioxidizing agent	1
Piccolyte S 85 resin (a thermoplastic resin of terpene) adhesion agent	50
Hexane	600
Naphtha solvent	5

Adhesive Formula 3:	Parts by weight
High molecular weight isobutyl polyvinylether, cohesion agent	45
Low molecular weight isobutyl polyvinylether, adhesion agent	40
Gum ester	5
Ethylene glycol	100
Heptane	200
Xylene	10

It is seen that the adhesive of the above formulae contain as a non volatile fraction at least one polyvinyl alkyl ether or a natural or synthetic rubber, while, their volatile fraction comprises at least one liquid aliphatic or aromatic hydrocarbon.

All the hereabove described adhesives have a high superficial adhesive effect which oppose the adjustment of the ink signs or even causes undesired effects of adhesion and transfer.

According to the present invention, the superficial adhesive effect is eliminated by causing the so-called flooding or horizontal floatation of a very thin layer of very fine powder at the exposed surface of the adhesive.

To act efficiently, said powder layer should isolate the adhesive mass from any direct contact with the receptor surface without reducing in any way the properties of the underlying adhesive mass. If the powder remains embedded within the adhesive, the superficial adhesive effect will remain unless the amount of powder is such that a reduction of superficial adhesive effect will be the result of a corresponding reduction of the adhesive properties of the whole adhesive mass, which would be contrary to the aimed object.

Neither is it possible to obtain satisfactory results by spraying powder on the adhesive after application of the latter because this operation does not allow to adjust the amount and uniformity of the powder layer's thickness.

According to the present invention, in order to provide a good floatation, the powder should meet the particles size and density requirements indicated above, namely:

particle size: maximum 50 millimicrons
particle specific gravity: below 3.

For reasons which will appear hereinafter, it is also essential that the refractive index of the powder material be below: 1.7 and it is important that the powder be translucent.

Materials which in powder form meet these requirements include:

synthetic silica: specific gravity 2.4; refractive index 1.50
synthetic silicates such as calcium silicate: specific gravity 2.60; refractive index 1.53
precipitated calcium carbonate: specific gravity 2.07; refractive index 1.55.

Without intending to limit his invention to any theory, applicant is of opinion that the floatation phenomenon concerning powder particles in adhesive is much analogous to what occurs in a pigment mixture in paint and varnish.

The evaporation of solvents from adhesive after application of the latter onto the surface of the provisional support and onto the ink signs is accompanied with a strong internal agitation which is shown by ascending

and whirling streams the magnitude and the frequency of which depend upon the amount of molecules of liquid contained in the adhesive as well as the thickness of the deposited layer. These ascending and whirling streams cause the powder to float at the surface of the adhesive. As the solvents evaporate, the superficial adhesive effect disappears and the adhesive seems to lose part of its transparency. This phenomenon develops uniformly and is much like the "horizontal floatation" or uniform color change which happens in a paint film when still wet. The disappearance of the superficial adhesive effect and the transparency of the adhesive probably are due to the surface concentration of several thicknesses of powder particles imperfectly moistened by the low molecular weight phase of the adhesive.

The deformation of the adhesive under the action of a suitable pressure increases the molecular agitation. As a result thereof, the adhesive molecules slide between the powder particles which again become perfectly wetted and are dispersed again within the adhesive. Indeed, the adhesive is seen to recover its transparency.

It should be understood that such phenomenon depends upon the concentration of powder in the adhesive. Beyond a certain concentration, the adhesive mass recovers less and less its initial transparency and a reduction of the adhesive properties is seen at the same time. The adhesive medium seems indeed to have no longer the power needed for perfectly wetting all powder particles.

The evolution of the adhesive transparency is evidence of the disappearance and the appearance of the superficial adhesive effect. This explains the importance of optical properties such as refractive index and translucency of the powder incorporated with the adhesive.

The process conditions in connection with the adhesive according to the present invention are given hereinafter:

1st—The pressure-sensitive adhesive is applied onto the provisional support and the ink signs by a process such as silk screen which makes it possible to deposit a layer whose thickness is not below 20 microns before evaporation of the solvents. The thickness of the adhesive layer should be equal to or greater than 5 microns after evaporation of the solvent. Therefore, the ratio of the weight of the volatile fraction to the weight of the non volatile fraction should be at least of 3:1.

2d—One obtains under the best circumstances the disappearance of the superficial adhesive effect when the ratio of the weight of the powder to the weight of the volatile fraction is at least of 1:45.

3d—One obtains under the best circumstances the re-appearance of transparency and superficial adhesive effect under a pressure when the ratio of the weight of the powder to the weight of the non volatile fraction is at most of 2:5.

The pressure necessary for transferring the ink sign depends upon the latter ratio as well as on modifications of the rheological properties of the adhesive due to the migration of the fluidity agent. In order to cause migration of the fluidity agent in the adhesive, it has been found sufficient for the adhesive to contain volatile materials without true solvating action on the ink polymer, so as to cause a slight swelling in the surface area of the ink film. Thus, it has been found that on an ink sign of nitrocellulose nature (ink Formula 1), a contact of very short duration was necessary to bring about the migration of stearate in an adhesive containing aliphatic solvents such as benzine or aromatic solvents such as toluene. The migration of ink fluidity agent into the adhesive above the ink sign modifies the rheological properties of the adhesive at that place in such a way that the adhesive covering the ink signs answers more easily when subjected to a pressure applied on the back of the provisional support, slides between the particles of powder, nets the latter and reaches the receptor surface to make

the ink sign adhere thereto. On the contrary, the adhesive mass located out of the ink sign has a higher threshold of deformation and goes a little, if any, through the layer of powder. The modification of the rheological properties of the adhesive above the sign also has for its effect to facilitate the shearing of the adhesive on the edge of the ink sign.

According to the intended use of the dry transfer material and the requirements of the user, it is possible, by increasing the concentration of the powder in the given limits and by varying the percentage of fluidity agent migrating into the adhesive, to make dry transfer materials by transferring perfectly an ink sign at a pressure between 50 and 350 g./mm.².

It is important to note that the powder particles contained in the adhesive have a relatively high capacity of absorbing oil and similar materials, in direct relation with their fineness. When pressure is applied onto the adhesive to make the superficial adhesive feature appear again, the particles are indeed wetted by the low molecular weight phase of the adhesive. The result thereof is a reduction of adhesive power of the adhesive. To compensate for this reduction it has been provided according to the present invention to increase the low molecular weight phase of the adhesive or to add to the adhesive a plasticizer such as tricresyl phosphate, ricinus oil, methyl abietate. According to this invention, the weight of added plasticizer is at least equal to twice the weight of powder mixed with the adhesive.

In the transfer material according to the present invention, the superficial adhesive properties appear under the effect of a pressure. It is thus necessary that said transfer assembly be protected before use by means of a protecting sheet having anti-adhesive properties. For this purpose, a silicone-treated paper sheet is used according to the present invention. The superficial adhesive action of the adhesive having disappeared the protecting sheet cannot even slightly adhere to the adhesive.

In order to avoid that the protecting sheet slides or be shifted during handling preceding use of the transfer material, it is necessary that the protecting sheet be attached to the support or carrier by means of pressure-sensitive adhesive tapes applied on at least one side of the support sheet as disclosed in Belgian Pat. No. 614,782, or by sewing, soldering or clipping.

The accompanying figure of drawing shows schematically, in section and at very great scale, a fragment of a dry transfer material according to the present invention.

On said figure of drawing, reference numeral 1 designates the provisional support sheet made, for example of polystyrene, on which an ink sign 2 is printed. The support or carrier sheet 1 and the ink sign 2 are covered with an adhesive layer 3. According to the present invention, the ink of sign 2 contains a non volatile oozing material 4 such as described above, concentrated at the upper surface of the sign and having exuded into the adhesive layer 3 when the latter has been brought into contact with ink sign 2. Also according to the present invention, the adhesive layer 3 has on its free surface, a layer 5 made of one or more strata of side by side placed particles of silica powder such as described above, said layer being formed by floatation of a silica powder contained within the adhesive, upon evaporation of the volatile fraction of the adhesive, after the latter has been applied onto the provisional support sheet 1 and the ink sign 2.

The non volatile exuding material 4 modifies the properties of the adhesive 3 above the ink sign 2, in such a way that under the action of a sufficient pressure, the adhesive located above the ink sign 2 may pass more easily than the adhesive located out of the ink sign, through the particles layer 5, wet the latter and reach a (not shown) receptor surface so as to make the ink sign 2 adhere selectively to said receptor surface.

7 EXAMPLE

Onto a provisional support comprising a polystyrene sheet of 800 mm. length, 400 mm. width and 0.12 mm. thickness, a series of ink signs are printed by a silk screen process using a clear ink based on nitrocellulose, according to ink Formula 1 given above.

After printing of the ink signs and before applying an adhesive onto the polystyrene sheet, the latter is passed through an apparatus of the EL-1 type, available from the German firm DEMES, in order to modify by an ion bombarding in high tension alternating electric fields the polarity characteristics of that face of said sheet which will receive the ink signs, so as to provide a better bonding of the adhesive to the polystyrene. A pressure-sensitive adhesive of the polyvinylether type according to adhesive Formula 1 given above is applied as a 24 micron layer, said adhesive containing, per 445 parts by weight of adhesive, 100 parts by weight of a non volatile fraction in the form of polyvinylether and 300 parts by weight of a volatile fraction, the latter comprising a mixture of toluene, benzine (100/140) and heptane in the proportions indicated above in adhesive Formula 1. According to the present invention, the adhesive contains, in addition, 15 parts by weight of pyrogenated silica powder having a particle size between 5 and 20 millimicrons, a specific gravity of about 2.4 and a refractive index of about 1.5. In addition, the adhesive contains, also according to the present invention, about 30 parts by weight of ricinus oil as a plasticizer.

Onto an identical support, the same adhesive but without silica powder is applied under the same conditions, as a control.

After drying of the adhesives on their respective supports, the superficial adhesive characteristic of the adhesive in the provisional support-ink sign-adhesive material according to the present invention is caused to appear or revealed by rubbing by means of a hard tool. Thereafter the optical densities in white light respectively of the control adhesive, the revealed adhesive and the not revealed adhesive are measured using an optical densitometer, with the following results:

	Percent of transmitted light
Control (pure) adhesive	96.5
Revealed adhesive	96.0
Not revealed adhesive	85.0

The difference of transmitted light between revealed and not revealed adhesives indicates the formation of a very thin layer of powder obtained by floatation. The almost identical values for the control adhesive and the revealed adhesive show that the powder concentration did not appreciably influence the transparency. Moreover, the superficial adhesive effect of the control adhesive is seen to be identical with that of the revealed adhesive.

Using a dynamometer, it is seen that a pressure of 220 g./mm.² should be applied during 20 seconds to provide a transfer of the ink sign and that under such pressure and during that time, the adhesive molecules overlapping the ink sign do not reach the receptor surface.

What I claim is:

1. A process for making a dry transfer material comprising (a) providing a light-transmitting support sheet which has a surface of synthetic polymeric material with a critical surface tension less than 37 dynes/cm., (b) placing on said surface ink signs which contain, a non-volatile liquid of molecular weight below 600 capable of diffusing from said signs through the surface thereof opposed to their surface of contact with said support sheet, said liquid being a plasticizer for pressure-sensitive adhesive (c) covering said surface of said support sheet with a pressure-sensitive adhesive layer having in itself great adhesiveness once it is dried, the adhesive of said

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adhesive layer being applied as a composition comprising a volatile fraction of at least one member selected from the group consisting of aliphatic liquid hydrocarbons and aromatic liquid hydrocarbon and a non-volatile fraction of at least one member selected from the group consisting of polyvinylalkylether, natural rubber, and synthetic rubber in a weight ratio of at least 3:1, said adhesive composition also containing solid particles of silica having a size between 5 and 20 millimicrons, a specific gravity of about 2.4 and a refractive index of about 1.5, the weight ratio of the solid particles to the volatile fraction of said adhesive composition being at least 1:45 and the weight ratio of the solid particles to the adhesive composition being at most 2:5, said adhesive composition further containing a plasticizer in an amount such that the weight of said plasticizer is equal to at least twice the weight of said solid particles, said solid particles having neither a chemical nor physical effect on said adhesive composition, (d) drying said adhesive composition and thus causing said solid particles to be drawn towards the outer surface of the adhesive layer under the action of evaporation of the volatile fraction to form a substantially non-tacky layer of several superimposed strata of solid particles at said outer surface whereby the underlying adhesive layer keeps its great adhesiveness (e) reducing the viscosity of said adhesive layer in the areas above said ink signs with respect to the remaining adhesive layer by diffusion of said non-volatile liquid from said ink signs into said adhesive layer in said areas.

2. A process according to claim 1, wherein said non-volatile diffusing liquid is selected from a group consisting of di(2-ethylhexyl) azelate, butyl stearate, triethyl phosphate castor oil and whereas said plasticizer contained in the adhesive is selected from a group consisting of tricresyl phosphate, castor oil and methyl abieate, and after applying ink signs and before applying the adhesive layer, the surface polarity of the support sheet is modified to increase the bond between the adhesive layer and the support sheet in those areas where the surface is free of ink signs.

3. A process as in claim 1 wherein said ink signs contain a cellulose ester and said non-volatile liquid capable of diffusion from said ink signs comprises butyl stearate and castor oil.

4. A process as in claim 1, wherein said ink signs contain a polyvinyl butyral and said non-volatile liquid capable of diffusion from said ink signs comprises di (2-ethylhexyl) azelate.

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