In the particular embodiments described in the specification, hot melt inks (110, 120) for colored ink jet images are described which have relatively narrow melting ranges while at the same time inhibiting crystallinity upon quenching to reduce attenuation of transmitted light. In addition, the inks (110, 120) intended for application to the same substrate have matched surface tensions at the temperature at which they are maintained above their melting point on the substrate to avoid mingling of different inks at their interfaces. Furthermore, the inks have an elongation of at least 3 %, and preferably about 5-10 %, so as to avoid delamination from a transparent substrate despite relatively low adhesive strength of the ink to the substrate.
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Description

Hot Melt Inks for Colored Ink Jet Images

Technical Field
This invention relates to hot melt inks for producing colored images by ink jet printing and, more particularly, to new and improved colored hot melt inks providing improved image quality.

Background Art
To produce black-and-white images by projection, it is only necessary for the transparency to attenuate or prevent light from being projected to the screen in the appropriate areas. For color projection images, however, the ink must block or attenuate only selected wavelengths of the light and must permit the other wavelengths to be projected to the screen. Where water-based inks are utilized, the image on the transparency is substantially flat so that the only factor affecting the transmission is absorption of the appropriate colors of light. Where hot melt inks are used, however, the ink drops form hemispherical lenslets which, as described in the Fulton et al. Patent No. 4,873,134, interfere with the proper reproduction of projection images from a color transparency. As described in that patent, this problem may be overcome by causing the ink drops to spread on the substrate to reduce the curvature of the lenslets.

There are, however, additional problems encountered in the formation of color images with hot melt inks. For example, in order to assure that all of the ink drops are formed and projected in substantially the same way, the various colored inks should have certain similar physical properties and characteristics even though they are not comprised of identical components in identical proportions. For optimum
quality, all of the colored inks must be substantially transparent at the appropriate wavelengths even though some of the inks may contain pigment while others contain dye, and the vehicle for the ink should be substantially colorless.

One problem encountered in hot melt inks is the tendency for the ink vehicle to become substantially crystalline upon solidification since a significant crystalline content will interfere with the transparency of the ink. On the other hand, it is desirable that the ink vehicle soften at as high a temperature as possible so that it is not subject to softening in extreme ambient conditions such as the trunk of an automobile in summer or the platen of an overhead projector. In contrast, however, it is also desirable that hot melt inks melt at a temperature which is sufficiently below the jetting temperature that the inks have a relatively low viscosity, typically in the range of 10–30 centipoise, at the temperature of application. If the application temperature is too high, such as above about 140°C, the printhead materials will be subjected to undue thermal stresses and the inks may age quickly. Moreover, as described in the copending application of Spehrley, No. 07/202,488, filed June 3, 1988, the rheology of the hot melt inks above the melting point should be controlled so as to facilitate good spreading of the ink drops on or into the substrate.

Furthermore, when different colored ink drops are maintained above their melting points on a substrate to permit spreading in accordance with Patent No. 4,873,134, it is important that the rate of spreading of the different colored drops be substantially uniform in order to assure not only the desired coverage of different inks on the substrate, but to avoid undesired intermixing of different-color drops, which can cause severe image quality degradation.
Finally, solid hot melt inks must have a compliance which is compatible with that of the substrate on which they are printed so that, when the substrate is folded or bent, the inks will not crack or separate from the substrate.

Disclosure of Invention

Accordingly, it is an object of the present invention to provide new and improved hot melt color inks which overcome the above-mentioned disadvantages of the prior art.

Another object of the invention is to provide a set of hot melt color inks having substantially matched characteristics.

A further object of the invention is to provide hot melt color ink images of high quality.

These and other objects of the invention are attained by providing hot melt inks having relatively narrow melting ranges, i.e., differences between liquidus and solidus temperatures, while at the same time having low crystallinity when solidified by rapid cooling. Moreover, a set of different colored hot melt inks according to the invention have surface tensions which vary by no more than about 3 dynes per centimeter, and preferably no more than 2 dynes per centimeter at the temperature at which they are held for spreading on the substrate. Finally, each of the different colored hot melt inks of the invention has an elongation of at least 3%, and preferably about 5-10%, to provide a compliance or flexibility at room temperature which permits bending of a substrate containing the ink to a radius of 0.10 to about 0.03 inch (2.54 to about 0.76mm) without causing fracture or flaking of the ink.

Brief Description of Drawings

Further objects and advantages of the invention will be apparent from a reading of the following de-
scription in conjunction with the accompanying drawings in which:

Fig. 1A is a graphical representation illustrating a differential scanning calorimeter curve of absorbed energy per degree versus temperature for a hot melt ink having desired characteristics;

Fig. 1B is a graphical representation showing variation of viscosity with temperature for the ink of Fig. 1A;

Fig. 2A is a graphical representation of a differential scanning calorimeter curve of absorbed energy per degree versus temperature for an ink showing high crystallinity;

Fig. 2B is a graphical representation of the viscosity versus temperature characteristic of the ink of Fig. 2A;

Fig. 3A is a graphical representation showing a differential scanning calorimeter curve for an ink having relatively amorphous characteristics with low crystallinity;

Fig. 3B is a graphical representation of the variation of viscosity with temperature for the ink of Fig. 3A;

Fig. 4A is a schematic illustration showing the light transmission characteristics of an ink drop on a transparent substrate;

Fig. 4B is a graphical representation showing the attenuation of light as a function of thickness of ink for an ink of different crystallinity;

Figs. 5A-5D illustrate successive stages in the spreading of hot melt ink drops maintained on a substrate at a temperature above their melting point;

Fig. 5E is an enlarged view illustrating the overlap of two adjacent drops before spreading on the substrate;

Figs. 6A-6E are schematic illustrations showing the spreading and overlap of adjacent drops maintained above their melting point on a substrate;
Figs. 7A and 7B are enlarged views similar to Figs. 6A and 6B illustrating the elimination of overlap of adjacent drops upon spreading on a substrate; and

Fig. 8 is a fragmentary cross-sectional illustration showing an ink image on a transparent polyester substrate;

Fig. 9 is a fragmentary view showing the ink and substrate of Fig. 8 when bent to provide a curvature;

Fig. 10 is a graphical representation showing the maximum shear stress against the bending radius for ink on a substrate of the type shown in Fig. 8;

Fig. 11 is an enlarged fragmentary view illustrating the contact angle at the edge of an ink region on a substrate; and

Fig. 12 is an enlarged fragmentary view showing an ink layer on a substrate subjected to bending in which the ink layer has become torn to create a sharp edge.

Best Mode for Carrying Out the Invention

The melting and rheological characteristics of a hot melt ink may be understood by reference to two graphical relationships, i.e., the differential scanning calorimeter ("DSC") curve of absorbed energy per degree versus temperature and the curve of viscosity versus temperature. In Fig. 1A, the curve 1 illustrates representative DSC data for a hot melt ink of the type which normally has moderate crystallinity. Conventionally, this curve is simplified by fitting the data with four straight lines, a line 2a which indicates the change in specific heat with temperature below the melting range, a line 2b which indicates the change in specific heat with temperature above the melting range, a line 3 which indicates the change of specific heat with temperature from the maximum \( T_M \) to the liquidus temperature \( T_L \) where the line 3 intersects the line 2b, and a line 4 representing the
change of specific heat with temperature between the maximum temperature $T_M$ and the solidus temperature $T_S$ at which the line 4 intersects the line 2a. The entire range from $T_S$ to $T_L$ is designated as the melting range, and the melting point $T_M$ is represented as the temperature at the intersection of the lines 3 and 4.

While all hot melt inks soften with increasing temperature as shown by the curve in Fig. 1A, the typical hot melt ink softens very rapidly above the solidus temperature $T_S$ up to the melting point $T_M$, and, above the temperature $T_M$, there is a liquid fraction but the ink may not pour or have a viscosity of the conventional type until the temperature is substantially above $T_M$. At temperatures above the liquidus temperature $T_L$, the ink is completely liquid (except for pigments) and has a viscosity versus temperature relationship represented by the line 6 in Fig. 1B.

Hot melt inks are jetted at a temperature $T_J$, a temperature which is substantially above the liquidus temperature, where the viscosity of the ink is in the range of, for example, 10-30cps and the slope of the viscosity line 6 is low. When hot melt inks deposited on a substrate are cooled, the viscosity of the inks increases slowly in the direction of decreasing temperature along the line 6 and then more rapidly along a line 7 and finally reaches a point where the viscosity is unmeasurable by conventional techniques in a region designated 8.

As described in the copending application of Spehrley, No. 07/202,488, filed June 3, 1988, once the viscosity of a hot melt ink has reached a level above about 200cps upon cooling, the ink spreads on or penetrates a substrate at such a low rate as to be essentially immobile. This spread-limiting temperature is designated $T_{SL}$ in Fig. 1B, and the difference between the temperature $T_{SL}$ and the jetting temperature $T_J$, denoted $\Delta T$ and called the spreading temperature, determines the enthalpy available in each ink droplet.
to provide heat so as to cause self-spreading of the ink on or into the substrate. Since it is desirable for the ink to spread to a relatively large extent on or into the substrate, it is important to have a large $\Delta T$ between the jetting and the spread-limiting temperature, and for the viscosity to remain as low as possible throughout this temperature range. Because of printhead material limitations, however, it is not practical to achieve such large $\Delta T$ by increasing printhead temperatures significantly above about 125°C.

In order to obtain the highest softening point and the largest spread between the jetting temperature $T_J$ and the temperature $T_{SL}$ at which spread-limiting viscosity is reached, an ink having a DSC curve of the type illustrated in Fig. 2A would be desirable. Such inks have narrow melting ranges, i.e., $T_L - T_g$, but they tend to be more crystalline and therefore less transparent after solidification than inks having a broader melting range, while the energy available to spread the ink as indicated by $\Delta T_1$ in Fig. 1B is larger than that of the ink shown in Fig. 1B.

Hot melt inks which are amorphous in character and therefore more transparent after solidification have a broad melting range of the type illustrated in Fig. 3A. Such inks start to soften at a relatively low temperature, making them less durable at mildly elevated temperatures. Moreover, the jetting temperatures for such inks may have to be increased to levels above the maximum desirable printhead temperatures in order to obtain a low enough jetting viscosity. In addition, the enthalpy available in each drop for self-heated spreading, represented by $\Delta T_2$, is normally significantly less for inks of this type than for the inks of Figs. 1A and 2A.

From the foregoing, it should be apparent that, considering the combined aspects of ink durability, reasonable jetting temperature and enthalpy available
for self-spreading of ink, a very narrow melting range ink material is desirable. For example, a hot melt ink having a melting point of at least 75°C, a melting range of no more than about 40°C, and a spreading temperature range of at least 30°C is preferable. However, such narrow-range materials are normally more highly crystalline than broader melting range inks and crystallinity renders the inks unsuitable for use in transparencies because of the poor ink transparency in the solid state.

Crystallinity of solidified hot melt inks results in two detrimental effects, i.e., surface losses and bulk transmission losses. Microscopic examination of a crystallized hot melt ink drop shows a surface which looks "frosty" and which produces significant scattering of light passing through the drop. Internal crystallinity reduces the bulk transmission coefficient of the drop by causing scattering of light within the interior of the drop.

The importance of reducing such detrimental effects of crystallinity in inks will be understood by reference to the schematic illustration of Fig. 4A which shows a cross-section of a transparency with an ink drop illuminated with light normal to the surface of the transparency. The ink drop has a small contact angle with the surface of the substrate as a result of having been maintained above its melting point in the manner described in Patent No. 4,873,134, and, because of the small contact angle, it will be assumed in the following discussion that light is transmitted in substantially straight lines through the drop rather than being deviated by refraction of the surface of the drop.

The light $I_0$ which is incident on the portion of the transparency substrate having no ink drop is transmitted with some intensity reduction due to index of refraction mismatch to an observer but without any variation in the spectral content of the light. In
other words, the light $I_1$ will be perceived as "white" by the observer. In contrast, the light passing through the ink drop is selectively attenuated, the attenuation being a function of both the thickness of the ink and the absorption of light of different colors $x,y,z$ by the ink. The light is also attenuated by scattering $I_5$ as a result of any "frosting" on the surface of the ink drop and crystallinity within the drop. The ratio of the intensity $I_2$ of the resulting light beam passing through the drop to that of a light beam $I_1$ which does not intersect the drop is a measure of the optical properties of the ink drop. Each of these attenuation mechanisms is explained in more detail hereinafter.

Fig. 4B illustrates the measured attenuation of light of a specific wavelength or color as a function of thickness. Lambert's Law predicts that the logarithm of the attenuation will be linear with thickness and this is generally true for the low colorant loadings typical of transparent hot melt inks. The three diagonal lines 10, 11 and 12 shown in Fig. 4B represent three different ink conditions. The lowest line 10 represents an ink that was maintained above its melting point for a period of time and then caused to cool slowly with a cooling or "quenching" rate on the order of 0.02°C per second. The middle line 11 and the upper line 12 show that the attenuation of ink is reduced by increasing the rate of quenching of the ink, the middle line 11 indicating the attenuation when the ink is cooled at a rate of 20°C/sec. and the upper line 12 indicating the attenuation when the ink is quenched, for example, in ice-water at a rate of 40,000°C/sec. For high-quality color reproductions, the attenuation of the ink at the desired wavelengths should be less than about 25%, and preferably less than about 10%, which can be achieved based on the illustration in Fig. 4B if the ink is quenched at a
rate of at least 500°C/sec., and preferably at least 1,000°C/sec.

By extrapolating the lines 10, 11 and 12 on Fig. 4B back to zero thickness, i.e., the ordinate axis, the respective intersections 13, 14 and 15 indicate that there is some attenuation not dependent on the thickness of the drop, which corresponds to the surface losses resulting from a "frosty" crystallinity on the surface rather than the bulk losses resulting from crystallinity within the drop.

In order to provide a hot melt ink which has the lowest possible attenuation at high quenching rates, the ink vehicle should include a constituent which tends to prevent the molecular chains in the vehicle from moving into their preferred crystalline orientation during the quenching period. For this purpose, about 1-25 weight percent of a vehicle crystallinity modifier such as a branching polymer or resin or a crosslinked polymer or resin is added to the ink vehicle. Alternatively, the vehicle crystallinity modifier may be a small amount of a polymer or resin which is greatly mismatched (i.e., by 50-100 times) in size or effective volume with respect to the basic vehicle material. Such a relatively small proportion of modifiers such as branching polymers or crosslinked polymers or mismatched material need not significantly alter the DSC curve of the vehicle, but the presence of high molecular weight polyamides such as those having a molecular weight above 10,000 which are known to be viscosity modifiers should be avoided.

Typical vehicle crystallinity modifiers added for the purpose of providing reduced attenuation upon rapid cooling or quenching include ester-modified montan waxes, i.e.,

$$\text{RCO}_2-(\text{CH}_2)_n-0 \cdot \text{C-R}$$

in which R' and R are alkyl chains with 25-35 carbon atoms and n is an integer. Such materials are described, for example, in Patent No. 4,851,045, but
that patent does not suggest the use of such materials for reducing crystallinity.

In addition, the tendency of the vehicle to crystallize may also be reduced by the addition of petroleum ceresin waxes, as described, for example, at page 252 in The Chemistry and Technology of Waxes by A.H. Warth (1947). Also, based on the discussion at page 246 of Warth, it should be possible to use microcrystalline waxes such as the "pale yellow" microcrystalline wax melting at 85-87°C to improve quenching so as to reduce the light attenuation of rapidly quenched hot melt inks resulting from crystallization. Other materials discussed in Warth and in Bennett, Industrial Waxes, Vol. I (1975), pp. 281-283, include ketones such as stearone and laurone, which have a spatial configuration similar to that of the microcrystalline waxes and which do not deteriorate on storage.

Another characteristic of hot melt inks which is necessary to provide high-quality color hot melt ink images is the ability of the ink to spread to the desired extent while it is maintained above its melting point, as described in Patent No. 4,873,134, without causing interference with adjacent ink drops, for example, by bleeding of one color ink drop into an adjacent drop of a different color.

In Figs. 5A-5D, a series of illustrations shows the sequence of hot melt ink drops 100 jetted onto a nonporous substrate, solidified, and then later maintained above the melting point for a short period of time. In Fig. 5A, the drops are illustrated within a few milliseconds of application to the substrate. In Fig. 5B, the condition of the drops within a few hundred milliseconds is shown, indicating that the first drops 100 have partially spread and solidified and that a second set of drops 101 is deposited adjacent to the first set of drops. In Fig. 5C, the condition of all of the drops after several hundred milliseconds when all of the drops have solidified is shown. In
this illustration, an isolated droplet 101 has solidified with a large contact angle which will cause undesired refraction of the light passing through the drop.

In Fig. 5D, the condition of the ink drops is shown after they have been maintained above their melting point for a selected time period in accordance with Patent No. 4,873,134 to reduce the contact angle of the drops with the substrate. According to a preferred embodiment, a 95-picoliter drop will have spread to produce a drop diameter of about 8-9 mils (0.20-0.23mm) with a contact angle of about 5-7° after being maintained for about 3 seconds at a temperature of about 100°C, which is about 10°C above the liquidus temperature of the ink, and for single drops, the spread diameter is relatively insensitive to surface tension in the range 27-30 dynes per centimeter. Although the droplet has not spread to its equilibrium diameter after that period of time, the rate of ink spread is very slow and, if it were maintained at that temperature for 30 seconds, the diameter would increase only a few percent more and after several minutes at that temperature, there would be little further noticeable spreading.

With a conventional polyester substrate having a surface tension of about 35 dynes per centimeter and a hot melt ink having a surface tension of about 27-30 dynes per centimeter, the average rate of spreading of a drop of molten ink on the substrate during the first three seconds is about 1 mil per second. Surprisingly, however, the spreading velocity of ink at the intersection of two coalesced groups of ink drops, such as the fields 110 and 120 in Fig. 5D, can be 10-20 times greater than the spreading velocity of a single drop. As a result, whereas a single drop will spread within a desired maximum range while held at a temperature above its melting point for a short period such as 3 seconds, two adjacent ink fields 110 and 120
may spread into each other to a much greater extent, such as 10-25 mils (0.25-0.63mm) or more, during the same period of time, causing undesired bleeding and intermixing of different colored inks.

There appear to be at least two sets of phenomena which must be controlled to prevent such objectionable intermixing at the boundaries of color fields. Intermixing due to diffusion-like phenomena is one phenomenon, and is related to miscibility and chemical concentration differences, and perhaps to pigment sizes. Such diffusion-like intermixing appears to be limited to dimensions on the order of 1-2 pixels (3-6 mils (0.076-0.15mm)) during the times of interest (i.e., about 3 seconds) and are much less objectionable in projection images than the second type.

The second type of intermixing occurs to a much greater extent (about 10-25 mils (0.25-0.63mm)) and is caused by surface tension mismatch effects, which provide the driving force to create ink flows, the resistance to such flow being produced by viscous resistance which is a strong function of fluid thickness, as will be further described.

Fig. 6A shows an enlarged view of the region 103 of Fig. 5C when the ink has not been maintained above its melting point for a selected period of time such as 3 seconds. In this case, ink from the coalesced field 120, which has a surface tension of about 30 dynes per centimeter, is illustrated at the instant of melting along with ink from an adjacent field 110 having a lower surface tension such as 25 dynes per centimeter. Both fields are printed on a polyester substrate which typically has a surface energy of about 35 dynes per centimeter. In Fig. 6B, which illustrates the condition after the inks have been maintained above their melting point for a few hundred milliseconds, it will be seen that the ink from the field 110, which has a lower surface tension, wets and flows over the ink from the field 120 having the
higher relative surface tension. Fig. 6C shows the overlap condition after the inks have been maintained above their melting point for a longer period of time, producing substantial intermixing of the inks which is detrimental to the image quality. Although these figures illustrate the intermixing as being substantially two-dimensional, there are important three-dimensional effects. In particular, the lower-surface-tension ink 110 tends to be drawn more quickly into the interstices between original droplets where the curvatures are greater.

Prior efforts to prevent such bleeding and intermixing of adjacent fields of molten ink have not been successful. For example, orienting the substrate in such a way that gravity inhibits flow of the low-surface-tension ink in the direction toward the higher-surface-tension ink has not avoided the problem.

In accordance with the invention, however, surface tension modifiers are utilized so as to keep the surface tensions of all of the inks applied to the same substrate within less than 3 dynes per centimeter and, preferably, within less than 1-2 dynes per centimeter at the temperature at which they are maintained above their melting point for a selected period of time. The result of such matching of surface tensions is shown in Figs. 7A and 7B. Fig. 7A illustrates the initial interface between two adjacent ink drops applied in succession, a drop 110 being applied after a drop 120. Both inks have a surface tension of 30 dynes per centimeter and the substrate has a surface energy of 35 dynes per centimeter. After being maintained above their melting point for a few seconds, the drops have an interface in the region 113 which may include some intermixing due to diffusion, but which does not vary significantly from the original interface, and neither drop has spread over the other drop so as to cause undesired intermixing of the inks.
Surface tension modifiers are known, for example, from the Japanese Patent Publication of Ohta, No. 55-54368. It should be noted, however, that the surface tension modifiers used in hot melt inks for the purpose of avoiding bleed and intermingling of ink on a substrate in accordance with the invention may be different from those which are appropriate for controlling drop formation during ink ejection, which occurs in a matter of microseconds. For the purposes of the present invention, the surface tension modifiers should be effective on a time scale of a few seconds, such as 3-10 seconds. Such surface tension modifiers are fatty acids or salts (soaps), resin salts, salts of long-chain sulphonic acids, salts of long-chain alkyl ester sulphonates and the like, and they are characterized by being fairly similar in chemical nature to the materials commonly used in successful hot melt inks and by being ionic, although some nonionic versions of these materials may be useful in certain hot melt ink formulations. Also, the addition of paraffinic materials up to C25 materials may be expected to lower the surface tension of the vehicle and the molecular weight of such materials would tend to maintain the DSC melting point and durability of the ink vehicle. In fact, any soluble hydrocarbon with a surface tension less than that of the vehicle will tend to lower the surface tension of the ink.

Most importantly, the surface tensions of the inks applied to the same substrate in accordance with the invention must be matched at the temperature at which the inks are maintained on the substrate for a short period of time, as described in Patent No. 4,873,134. This may be different from the surface tension at the jetting temperature, which is the surface tension considered to be significant in prior art disclosures such as that of the Ohta Japanese Patent Publication No. 55-54368.
Finally, it is also important that hot melt inks used for preparing transparencies be essentially immune to flaking, peeling or otherwise partially delaminating from the surface of the transparent substrate. The difficulty encountered with hot melt inks is entirely different from that of water-based inks in which the carrier evaporates, leaving dyes or pigments dissolved into and chemically bound on a coating on the surface of the substrate.

For hot melt inks, the ink carrier or vehicle does not evaporate and the entire volume of the ink is maintained on the top of the smooth surface of the transparent substrate. Moreover, for subtractive color printing, two or more layers of ink may be overprinted to achieve a desired color and density. For example, to print a dark blue, a first layer providing complete coverage of a magenta ink may be completely overprinted with a second layer of cyan ink. The resulting ink film is relatively thick, being about 1 mil thick for a typical 95 picoliter droplet at the 300 by 300 spots per inch resolution typical of office printing.

Hot melt ink images printed on Mylar (polyethylene terephthalate) surfaces have been observed to flake and peel upon even gentle handling with some ink formulations. This problem is particularly associated with large solid area coverage, whereas other ink-related phenomena are associated with edges or lines of single dots. Moreover, the failures do not necessarily result in ink falling off the substrate surface, but ink images which have become partially delaminated from the substrate surface will project a noticeably darker image due to the two extra interfaces (between the ink/air and the air/substrate) in a delaminated region. Normally, one would expect to improve durability and resistance to flaking by increasing the bond strength between the ink and the substrate. This might be possible if a special coat-
ing for the substrate were provided which could mechanically or chemically bond to the ink. For example, the frosted surface of conventional polyester drafting material has a microtextured layer which effectively receives the ink and mechanically bonds to it, providing images which cannot be flaked off under even the most rigorous handling. Such surfaces, however, are too rough to be transparent and those images can be viewed only by reflection.

It might also be possible to provide a coating on the surface of the substrate which would enhance the chemical bond strength. Such an approach is well known, for example, since some commercially available films designed for use in transparency projection include special coatings of some sort to enhance the feedability and/or adhesion of xerographic toners or other liquid inks. Such approaches, however, require a specially prepared transparency substrate, whereas the present invention is capable of providing satisfactory results on any commercially available transparency substrate, such as, for example, Scotch Brand Types 503 and 8803 from Minnesota Mining and Manufacturing Company, Types 364-01-01 from Arkright, Types 174, 574, 688, 154 and 570 from 3M, Type 505 from ICI/Melinex and ordinary Mylar from Du Pont.

It has also been found that the flaking problem associated with hot melt ink applied to a transparent substrate cannot be overcome by increasing bond strength within the known limits of adhesive (lap shear) strengths of wax-like hot melt ink formulations.

Typical shear or peel strength data of a range of adhesive materials applied to transparent substrate materials are given in Table I.
TABLE I
Adhesive Strengths

<table>
<thead>
<tr>
<th>Adhesive to Base</th>
<th>Method</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desmocoll polyester to Mylar</td>
<td>Shear strength</td>
<td>138 psi (9.7 kg/cm²)</td>
</tr>
<tr>
<td>Polyurethane to Mylar</td>
<td>Peel strength</td>
<td>23 lb/in (4.1 kg/cm)</td>
</tr>
<tr>
<td>Tektronics thermal transfer ink to Tektronics film</td>
<td>Lap shear</td>
<td>27 psi (1.6 kg/cm²)</td>
</tr>
<tr>
<td>Tektronics thermal transfer ink to 3M #688 Mylar</td>
<td>Lap shear</td>
<td>51 psi (3.7 kg/cm²)</td>
</tr>
<tr>
<td>Spectra experimental ink #UL319 to Mylar (3M #688)</td>
<td>Lap shear</td>
<td>18-25 psi (1.26-1.76 kg/cm²)</td>
</tr>
<tr>
<td>Spectra experimental ink #UL249 to Mylar (3M #688)</td>
<td>Lap shear</td>
<td>100 psi (7.03 kg/cm²)</td>
</tr>
</tbody>
</table>

Fig. 8 shows a cross-section of a typical hot melt ink image stress condition, i.e., a large-area solid dark blue ink field on a 4-mil (0.1mm) polyester substrate 200 with an adjacent clear area. At 300-spot-per-inch resolution and with 95-picoliter drops, the dark blue area consists of a first layer of cyan ink 201 which covers 100% of the pixel sites and a second layer 202 of magenta ink covering 100% of the pixel sites, providing a total ink thickness of about 1 mil (0.025mm). Since both inks are of similar chemical composition and similar mechanical properties, it is convenient to simplify this to consider a single layer of ink 203 with uniform mechanical properties coated on a region of the substrate 200.

Flaking of the ink is caused by local deformation of the substrate to create an area of local curvature of radius R as illustrated in simplified form in Fig. 9. For typical materials and conditions \( t_f \), the thickness of the substrate, is 4 mils (0.1mm), \( t_i \), the ink thickness, is 1 mil (0.025mm) and, since Young's
Modulus E of the ink (being about 50,000 to 100,000 psi (3,515-7,030 kg/cm²)) is small compared to that of the polyester substrate (400,000-600,000 psi 28,120-42,180 kg/cm²), the neutral axis of the ink-substrate composite is very near the center of the substrate.

The shear stress at the interface 205 between the ink and the substrate is nearly zero everywhere except near the edge 204 where it rises to a peak value T which is represented in the graphical illustration of Fig. 10 for an abrupt edge. For durable hot melt inks, the Young's Modulus is about 50,000 psi (3,515 kg/cm²), and preferably 100,000 psi (7,030 kg/cm²) or larger. During normal handling it has been found that 4-mil (0.1mm) transparencies are subjected to deformation which produces local curvatures having a radius of curvature as low as 0.10-0.03 inches (2.54-0.76mm) and, for comparison, the radius at which "crease-whitening" occurs is only slightly smaller, being about 0.015 inch (0.38mm). Thinner sheets of 2-3 mil (0.5-0.75mm) thickness produce whitening at smaller curvatures, and thicker sheets produce whitening at larger curvatures. Nevertheless, it being an objective of the present invention to provide durable transparencies on commonly available substrate materials, it is necessary for the hot melt ink to withstand the stresses resulting from local curvatures as small as 0.10-0.03 inch (2.54-0.76mm) radius, which causes a shear stress of about 1,200 psi (84.4 kg/cm²) to 5,000 psi (351 kg/cm²), as illustrated in Fig. 10. According to Table I, however, materials suitable for hot melt ink are far weaker than these values and any time an abrupt edge such as shown at 204 in Fig. 9 occurs, the ink can be expected to delaminate from the substrate at small-radius curvatures, and the delamination can be expected to propagate until it reaches an area where the film curvature has an increased radius.

Fortunately, in printing processes wherein the inks are applied to a heated substrate in such a way
that they can self-spread or where they are maintained above their melting point for a period of time to permit spreading, as described in Patent No. 4,873,134, the edges of the ink areas which have spread produce a feathered edge with a contact angle 208, as shown in Fig. 11, which is less than 45°, and preferably as low as 5-7°, as described in Patent No. 4,873,134. Under these conditions, the shear stresses at the ink-film interface are reduced by an order of magnitude and the feathering is effective to prevent delamination at the edges.

On the other hand, delamination at abrupt ink edges such as indicated at 204 in Fig. 9 can be prevented only if the ink layer remains intact. As indicated in Fig. 9, the strain on the ink layer is given by

$$\varepsilon = \frac{t_i + t_f/2}{R}$$

In order for the ink layer to remain intact, it must be able to stretch under the same 0.10-0.03 inch (2.54-0.76mm) substrate curvature R as specified above, which requires elongation of at least 3%, and preferably about 5-10%, for a 1-mil-thick (0.025mm) ink layer. If the elongation capability of the ink is less than this, then it will tear and create a sharp edge 209, as shown in Fig. 12, from which delamination can propagate.

The capability of a layer of solid ink to elongate and thereby avoid delamination and tearing can be measured in bulk by common techniques such as "Instron" pull-testers, and the delamination resistance of such an ink correlates directly with that of thin jetted and remelted films which are bent over a test mandrel to produce specified curvatures.

In accordance with the invention, it has been determined that an ink elongation capability of at least 3%, and preferably 5-10%, is necessary to avoid delamination and tearing and also that the ink elongation capability must be maintained at very high strain
rates, since casual transparency handling conditions creates small creases and also produces strain rates which are as high as 25% per second and which may be as high as 100% per second as a result of vigorous handling or distortion of the transparency substrate.

Certain additives may be used to improve the elongation of hot melt inks. For example, acrylic resins or polyamides will increase flexibility and ethylene vinyl acetates provide good polymers to utilize at levels of about 4-20% because they tend to increase adhesion strength as well as elongation. These categories provide a wide range of specific materials from which to choose for particular inks and provide opportunities for obtaining good flexibility without sacrificing the matching of inks within an ink set with respect to viscosity and surface tension.

Where inks have been modified to achieve at least 3%, and preferably 5-10%, elongation before failure in accordance with the invention, we have found that transparencies made with such inks which have been maintained above their melting point in accordance with Patent No. 4,873,134 successfully withstand rough handling and avoid delamination even though the adhesive strength of the ink to the polyester substrate remains in the range of 20-100 psi (1.41-7.0 kg/cm²).

Although the invention has been described herein with reference to specific embodiments, many modifications and variations therein will readily occur to those skilled in the art. All such variations and modifications are included within the intended scope of the invention.
Claims

1. A hot melt ink having a melting point of at least about 75°C, a melting range of no more than about 40°C, and a spreading temperature range before solidification of at least 30°C.

2. A hot melt ink according to Claim 1 having a melting range of no more than about 30°C.

3. A hot melt ink having a light attenuation resulting from internal and surface crystallization of the ink of no more than about 25% following quenching of the ink at a rate of at least 500°C per second.

4. A hot melt ink according to Claim 3 having a light attenuation resulting from internal and surface crystallization of the ink of no more than about 10% following quenching of the ink at a rate of at least 1,000°C per second.

5. A set of hot melt inks to be applied to the same transparent substrate and maintained on the substrate at a selected temperature above the melting points of the inks, wherein the surface tensions of all of the inks at the selected temperature differ by no more than 3 dynes per centimeter.

6. A set of hot melt inks according to Claim 5 wherein the surface tensions of the inks differ by no more than about 2 dynes per centimeter at the selected temperature.

7. A set of hot melt inks according to Claim 5 wherein the surface tensions of the inks differ
by no more than about 1 dyne per centimeter at
the selected temperature.

8. A hot melt ink for application to a transparent
substrate having an elongation of at least about
3% at ambient temperature to inhibit delamination
from the substrate upon bending of the substrate.

9. A hot melt ink according to Claim 8 having an
elongation of at least 5% at ambient temperature.

10. A set of hot melt inks for application to the
same transparent substrate material to be main-
tained at a selected temperature above their
melting points for a selected period of time on
the substrate material comprising at least three
inks having different colors wherein the surface
tensions of the inks differ by no more than 2
dynes per centimeter at the selected temperature,
each of the inks having an elongation of at least
3% under ambient conditions and each of the inks
having an attenuation resulting from surface and
bulk crystallization of no more than 25% follow-
ing quenching at a rate of at least 500°C per
second.

11. A set of hot melt inks in accordance with
Claim 10 wherein each of the inks has a melting
range of no more than about 50°C.

12. A set of hot melt inks in accordance with
Claim 10 wherein each of the inks has a melting
point of at least 75°C.

13. A set of hot melt inks in accordance with
Claim 10 wherein each of the inks has a spreading
temperature range before solidification of at
least 30°C.
FIG. 10
**INTERNATIONAL SEARCH REPORT**

**I. CLASSIFICATION OF SUBJECT MATTER**

According to International Patent Classification (IPC) and to Patent Classification and IPC

- IPC(5): C09D 11/12 C09D 11/00
- US CL.: 106/31

**II. FIELDS SEARCHED**

<table>
<thead>
<tr>
<th>Classification System</th>
<th>Classification Symbols</th>
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<tbody>
<tr>
<td>US</td>
<td>106/31,30,27,22,20,273; 346/140R</td>
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</tbody>
</table>

*Documentation Search other than Minimum Documentation to the extent that such Documents are included in the Fields Searched.*

**III. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of Document</th>
<th>With indication, where appropriate, of the relevant passages</th>
<th>Relevant to Claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>US, A, 315,406 (SEIKO EPSON CORP.) 10 May 1989</td>
<td>See page 5, line 40.</td>
<td>1,2,5-7,10-13</td>
</tr>
<tr>
<td>Y</td>
<td>US, A, 4851,045 (TANIGUCHI) 25 July 1989</td>
<td>See col. 6, line 20-30.</td>
<td>1,2,5-7,10-13</td>
</tr>
</tbody>
</table>

* Special categories of cited documents:
- **Y** document defining the general state of the art which is not considered to be of particular relevance
- **E** earlier document but published on or after the international filing date
- **L** later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- **X** document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- **W** document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- **T** document member of the same patent family

**IV. CERTIFICATION**

- **Date of the Actual Completion of the International Search:** 15 APRIL 1991
- **Date of Mailing of this International Search Report:** 30 APR 1991

ISA/US

**TIMOTHY D. SAUNDERS**

Form PCT/ISA/210 (second sheet) (May 1986)
FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

- [ ] OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE

This international search report has not been established in respect of certain claims under Article 17(3) for the following reasons:

- [ ] Claim numbers  because they relate to subject matter not required to be searched by this Authority, namely:

- [ ] Claim numbers  because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

- [ ] Claim numbers  because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI - [ ] OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This International Searching Authority found multiple inventions in this international application as follows:

1. [x] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. [ ] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. [ ] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. [ ] As all searchable claims could be searched without effort, justifying an additional fee, the International Searching Authority did not invoice payment of any additional fee.

Remar. on Protest

- [ ] The additional search fees were accompanied by applicant’s protest.
- [ ] No protest accompanied the payment of additional search fees.