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ADHESIVELY ERADICABLE TRANSFER MEDIUM

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ABSTRACT OF THE DISCLOSURE

A transfer medium or typewriter ribbon is disclosed, which is capable of being utilized to imprint a letter and if the letter is erroneous, which is susceptible of adhesive removal. The ribbon is made of a hard, film forming resin with selective modification of its properties through the addition of additives which embrittle the film and make the resin more adherent for the imaging surface while not penetrating into the fibers of the paper imaging surface, and attaching itself. As time passes there is an increased attachment to the paper fibers thereby rendering a more permanent image.

COPENDING RELATED APPLICATIONS

Improved Adhesively Eradicable Transfer Medium, U.S. Patent Application Ser. No. 277,543 filed Aug. 3, 1972 in the name of Samuel D. Blair.

BACKGROUND OF THE INVENTION

This invention relates to transfer mediums and more specifically to typewriter ribbons.

Typewriting errors have occurred since the first typewriter was invented. The problem has been addressed in many ways including the development of an erasable bond paper which allows the erroneous letters to be manually erased using a normal pencil or typewriter eraser of a rubber or combination rubber and abrasive material. Other more recent techniques for correcting typewriting errors have included covering the erroneous letter or symbol to camouflage its appearance to give the general appearance of no error having been made. This is accomplished through one of several techniques. One technique which has been used is a liquid which contains a pigment or pigmented material carried in a volatile carrier fluid. This correction material is painted over the erroneous letter and allowed to dry thus adhering to the image sheet and providing a relatively unobtrusive correction. An alternate technique which has been used is that of a dry transfer material for covering the erroneous letter. The material is usually formed into a thin layer on a film or carrier sheet much the same as carbon paper and then used together with the impact of the erroneous letter to transfer a thin white layer or layer of other desired color onto the surface of the erroneous letter thus partially if not completely obscuring it from view.

There have in the past been disclosures relating to the correction of errors on a typewriter by use of an adhesive tape or adhesive material but the technique used resulted in the disruption of the surface of the image sheet in that fibers from the paper were literally pulled out of the sheet in order to adequately remove the erroneous image. This is required because the ink of the ribbons at that time had the capability of penetrating into the paper fibers and staining or permanently dyeing the paper upon printing and the fibers had to be physically removed from the surface of the paper to remove the image.

BRIEF DESCRIPTION OF THE INVENTION

The transfer medium, hereafter interchangeably referred to by ribbon or typewriter ribbon, is constructed using the residue of a solvent coated mixture to form a transfer layer, also referred to as the ink or ink layer. The ink layer is deposited upon a flexible thin supporting substrate. The solvent coated residue coating which makes up the ink is preferably formulated from a film forming resin which is hard rather than a waxy or friable resin and which is made brittle or frangible by the addition of a modifying agent, without softening the resin substantially. A second modifying material is added, if required, to make the ink layer releasable from the support substrate or film but yet still have a relatively high tendency to adhere to paper. The resin is preferably not substantially softened as softening will enhance smearing and smudging and promote adherence to the image sheet, resulting in poor error correction.

Correction of erroneously typed letters or symbols may be accomplished by adhesive removal from the surface of the image sheet or paper, using a piece of material having an adhesive surface, where the adhesive surface is impacted onto the erroneously typed letter. This adheres the adhesive surface of the correction material to the letter and when the correction material is pulled from the paper it pulls the letter with it. The resin used in the formulation of the ink layer as modified, must be cohesive to the point that it will hold the ink layer together for removal and not crumble, since the adhesive surface of the correction material is only in contact with one surface of the ink layer. If the resin has insufficient cohesive effect, only the exposed portion of the erroneous letter is removed and remainder of the image ink layer continues to adhere to the image sheet and thus leave a residue image. The cohesion of the ink layer must be greater than the ink layer's affinity for the paper or image surface. The ink layer must be formulated so that the adhesion is one of surface adhesion between the ink and the paper rather than a viscous penetration of the paper fibers or wetting of the paper fibers with the ink layer. Preferably no dyes are used in the coloring of the ink layer as dyes generally have a staining capability and stains and staining are to be avoided. Dyes mean only colorants which are soluble in the other components of the ink mixtures.

The adhesive correction materials which have been found to perform most advantageously are substrates preferably polyethylene terephthalate, which have been coated with a rubber or acrylic base adhesive. Generally speaking, silicone adhesive base materials appear to be only marginally operative or operative only on selected papers. Unless the adhesive attraction for the ink exceeds that of the ink for the paper, only partial removal of the erroneous character will occur.

OBJECTS OF THE INVENTION

It is the primary object of this invention to image symbols and characters on an image sheet that at the same time are readily correctable by impacting adhesive material into intimate contact with the letters or images.

It is another object of this invention to complement automatic erase or correction typewriting apparatuses with an adhesively correctable typewriter ribbon.

It is an additional object of this invention to image an image sheet from impact of a type font and provide an image which may be substantially completely removed by adhesive contact between a correction member and the image.

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of preferred embodiments of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The following explanation of the function of particular materials represents what is believed to be the best explanation in as much as the complete interaction is not fully understood.

The ink layer of the transfer medium or ribbon is compounded from carefully selected materials which provide the unique quality of being substantially, completely, adhesively removable from the image sheet onto which the ink has been transferred in the process of typewriting. The characteristics of the materials which are necessary to formulate a ribbon of the adhesively removable type are explained to the best of the understanding as it presently exists.

The primary constituent of the ink or ink layer of the correctable ribbon is a resin. The resin must be a hard resin rather than a waxy resin. Additionally, the resin must be of the type which is capable of solution in a solvent in order that the ink formulation may be deposited in a solution/dispersion form in a volatile carrier liquid.

To obtain the necessary cohesion in the ink layer it has been found that the resin should be of the film forming type which has a high degree of flexible integrity and is not so friable or flaky that it will flake or crumble similar to a wax. To obtain the necessary adhesion between the adhesive material and the ink, the resin must be readily wetted by most materials used to make pressure sensitive adhesive, i.e. rubbers and acrylics.

The resin preferably is of the form which although in contact with paper and paper fibers does not penetrate into the surface of the paper. This characteristic is important in that it allows the relatively easy removal of an erroneously typed letter.

The resin functions as the carrier, holder, or binder for other constituents of the ink layer.

Typical resins which possess the above properties include EAB 500–1, a cellulose acetate butyrate, marketed by Eastman Chemical Company; Vitel 222, a polyester marketed by Goodyear; Neocryl B–371, an acrylic copolymer marketed by Polyvinyl Chemicals; Emerez 3749 and Emerez 1530, each a polyamide marketed by Emery Industries and EAB 550, a more flexible cellulose acetae butyrate marketed by Eastman Chemical Company.

As one will readily recognize, each of the materials listed above has its own particular physical and chemical characteristics and although each is suitable as a resin around which to build an adhesively correctable ink mixture, each will not be equally advantageous in all circumstances, and may function differently on different papers.

The preferred resin is Emerez 1533 marketed by Emery Industries. Emerez 1533 is believed to be a diphenolic based polyamide having a softening point of about 98 to 102° C., viscosity at 160° C. of 26 to 34 poise, and an amine value of 5.2 miligrams KOH per gram and an acid value of 2.5 milligrams KOH per gram. Emerez 1533 also has a density of 8.3 pounds per gallon.

To modify any of the foregoing resins to provide them with an ultimate physical characteristic which is desirable, that of reduced tensile strength or film integrity, additives are included in the ink layer formulation.

To render the resin adequately frangible or brittle to provide sharp character definition upon impact by the type font, it is necessary to lower the tensile strength of the film formed by the resin when deposited from a solvent. It is desirable to avoid excessive softening of the resin as softening will make the resin more waxy or waxlike and reduce its removability from the paper surface. The weakening of the tensile strength or lowering of the tensile strength of the film formed by the resin appears to be as a result of the additive reducing the tendency for the polymer chains of the resin to intertangle. This reduced intertangling of the molecular chains in the resin reduces the film forming characteristic to the point where the film will break easily as compared to its unmodified state. The preferred modifying agent for reducing the tensile strength of the resin is a mineral oil. Mineral oils may be selected within a relatively wide range of viscosities and properties to accomplish the degree of modification necessary with each individual resin. A preferred mineral oil is Standard #34 Kyso white mineral oil sold by Standard Oil Company of Kentucky.

A second modifying agent is generally necessary to cause the ink layer to be less adherent with respect to the support substrate or film material upon which the ink layer is deposited to form the transfer medium. Generally such a film is a polyethylene film, but may be any other common film used in ribbon manufacture.

Preferably, the release properties may be imparted to the ink mixture by the addition during formulation of mixed octyl esters of fatty acids. One example of the appropriate esters which may be used to act as a release agent is a material marketed under the trade name "Plasticizer R–9–C 7025" by the C. P. Hall Company of Chicago, Ill. The Plasticizer R–9–C 7025 acts as a plasticizer in the more classic sense, in that it modifies the resin material such that it has an adherence to the paper which is enhanced but is not such that the adherence for the paper is so great that the images cannot be removed by being strongly contacted on the exposed surface by an adhesive coated substrate. Other known modifying agents include fatty acid esters type of plasticizers such as isopropyl palmitate and butyl stearate. These other agents react similarly to the Plasticizer R–9–C 7025.

Additionally, additives which are optional, in the sense that they are generally not required in every formulation but in selected formulations may be required, depending on proportions used or the specific characteristics of some of the materials, include an epoxy of the polyglycol diepoxide type. The addition of such a material, such as DER 736, an epoxy solution manufactured and distributed by Dow Chemical Company, is to further sharpen the edge definition of the images formed during the typing phase through the slight softening of the resin, while not reducing the capability to eradicate.

Another possible additive for the solution of an isolated problem includes the addition of a synthetic wax. Such a synthetic wax is Acrawax C manufactured by Glyco Chemicals. The addition of the synthetic waxes to the ink formulation has the effect of preventing oil migration to the ink surface when a large quantity of mineral oil is used as the hardening and embrittling additive. Oil migration creates handling problems and the ribbon will not feed properly in a typewriter. Such a quantity of mineral oil is, in some cases, necessary to adequately modify the resin, that there is a migration problem which will then result in surface concentrations of mineral oil.

In all formulations it is necessary to provide a coloring agent if the transferred ink layer is to be visible in contrast to the paper background. The preferred material for providing color includes carbon black. Other alternative materials, of course, would be different colored pigments which are not soluble in the modifying oils selected. Organic dyes may be used as pigments if they are insoluble in the modifying oils.

Humidity has been shown to be a strongly influencing factor in the manufacture of the adhesively correctable ribbon. The effect that humidity plays is not fully understood but is believed to be an effect on the film structure of the film forming resin as it is deposited from the solvent vehicle, while being dried, to form the ink transfer layer. It has been found that if the humidity is too high or too low, the eradication of the printed character is incomplete and unacceptable. It is believed that due to the evaporation of the solvent of the ink formulation, the temperature of the web when coated with the ink mixture is reduced to the point that a small quantity of moisture from the atmosphere condenses on the surface of the ribbon as it is being dried of the solvent mixture. The formation of the water droplets or moisture pockets on the surface of the ink layer are believed to affect the forma-

tion of a discontinuous film and also to affect the manner in which the materials of the ink formulation are deposited. Acceptable eradication results occur when the humidity in the manufacturing area is such that the film is coated with the ink mixture and then exposed to air containing from about .005 to about .012 pounds of water per pound of dry air. Best results have been obtained in the range of approximately .006 to .009 pounds of water per pound of dry air.

EXAMPLES

For the sake of simplicity in understanding the disclosure, a complete step by step preparation procedure for one formulation will be described with the understanding that the other formulations are prepared in the same or in an analogous manner using designated substituted materials, varied quantities, or substituted solvents. All constituents will be listed together with a percentage which represents the percentage of that constituent of the entire dry ink mixture or dry ink layer. The materials will be compounded in an analogous manner to that of the first example with adjustments being made with respect to quantities and proportionate amounts of solvents.

EXAMPLE 1

Solids	Percentage	Number of parts by weight
Resin (Emerez 1533)	28.6	30
Mineral oil (Standard #34 Kyso White Mineral Oil)	23.8	25
Plasticizer (Plasticizer R-9-C 7025)	19	20
Pigment (Mogul L)	28.6	30

The Emerez 1533 is dissolved in a solvent mixture of approximately five-sixths isopropanol and one-sixth toluene. The quantity of the blend used in the preparation of the resin solution is approximately two parts by weight of solvent blend to one part by weight of the resin Emerez 1533. Upon the completion of the dissolving of the resin, one part of carbon black and one part isopropanol are added for every three parts of the resin solution. This mixture is then ground for approximately 9 hours or until sufficient fineness of grind is achieved, and drained and filtered. A solvent blend having a solvent ratio of 3.4 parts isopropanol to one part toluene is prepared. To five parts of the above solvent blend, one part of Plasticizer R-9-C 7025 and 1.25 parts of Standard #34 mineral oil is added and thoroughly mixed. To this mixture 7.5 parts of the above dispersion and 11.5 parts of the solvent blend are added with stirring. This resulting mixture is then coated onto a substrate, preferably a three-quarter mil polyethylene high density film. The mixture is coated at 65° F. to 100° F., preferably at room temperature and to a coat weight of approximately 1.0 to 1.4 pounds per ream and dried in a dryer at a temperature of from approximately 100° F. to 140° F. Humidity is maintained at from about .006 to about .009 pounds of water per pound of dry air during the coating and drying operation.

Following generally the proportions described above in the formulating of the solvent blends with respect to the other constituents, the following examples may be formulated and the information given is the percent by weight of each constituent of the total overall dry ink coating.

EXAMPLE 2

	Percent
Mineral Oil (Nujol)	35
Resin (Emerez 1533)	35
Pigment (Mogul L)	25
Modifier (Acrawax C)	5

The above materials are combined using the techniques of Example 1 and made into a 20% non-volatiles components mixture with a solvent blend which is a 1:7 ratio of 1,1,1 trichloroethane, and isopropanol. This mixture is then cast on three-quarter mil high density polyethylene film and dried to form a transfer medium.

EXAMPLE 3

	Percent
Plasticizer (Isopropyl palmitate)	10
Mineral Oil (Standard #34)	25
Resin (Emerez 1533)	35
Pigment (Mogul L)	25
Oil Migration Preventer (Acrawax C)	5

This mixture is prepared according to the teachings of Example 1 and coated with a 20% non-volatiles solution of isopropanol, onto three-quarter mil high density polyethylene film.

EXAMPLE 4

	Percent
Plasticizer (Butyl Stearate)	10
Mineral Oil (Standard #34)	25
Resin (Emerez 1533)	35
Pigment (Mogul L)	25
Oil Migration Preventer (Acrawax C)	5

The above materials are combined with isopropanol to provide a 20% non-volatiles solution following the teachings of Example 1 and cast onto a three-quarter mil high density polyethylene film to form a transfer medium.

EXAMPLE 5

	Percent
Mineral Oil (Clearteck)	25
Resin (Emerez 1533)	45
Pigment (Mogul L)	25
Oil Migration Preventer (Acrawax C)	5

Following the techniques of Example 1 the mixture is combined with isopropanol to yield a 20% non-volatiles solution and coated onto three-quarter mil high density polyethylene substrate film.

EXAMPLE 6

	Percent
Mineral Oil (Clearteck)	29.2
Resin (Emerez 1533)	53.7
Pigment (Graphite)	9.8
Pigment (Mogul L)	2.4
Oil Migration Preventer (Acrawax C)	4.9

Again following the techniques of Example 1, the above materials are combined and formed into a 20% non-volatiles solution of isopropanol and cast on a three-quarter mil high density polyethylene film substrate to form the transfer medium.

EXAMPLE 7

	Percent
Plasticizer (Cochin Type Coconut Oil)	20
Resin (Emerez 1533)	50
Pigment (Neo Spectra A.G. Beads)	25
Oil Migration Preventer (Acrawax C)	5

This mixture is formed into a 20% non-volatiles solution with isopropanol and cast onto a three-quarter mil high density polyethylene film.

EXAMPLE 8

	Percent
Mineral Oil (Penteck)	5
Plasticizer (Texanol Isobutyrate)	40
Resin (Alcohol Soluble Propionate)	43
Pigment (Neo Spectra A.G. Beads)	12

The above materials are combined using the teachings of Example 1 with Ethanol to form a 20% non-volatiles solution and then cast on a .35 mil Mylar film to form a transfer medium.

EXAMPLE 9

	Percent
Resin (Emerez 1533)	35
Mineral Oil (Standard #34)	20
Plasticizer (Plasticizer R-9-C 7025)	15
Pigment (Mogul L)	25
Oil Migration Preventer (Acrawax C)	5
Epoxy (DER 736 Epoxy Solution), 1 part per 100 parts Solvent.	

Following the procedure of Example 1, a 20% non-volatile mixture is made using isopropanol and toluene, and coated to 1.8 pounds per ream and oven dried at 120° F. on a ¾ mil polyethylene sheet. The resin is dissolved in a 5:1 isopropanol/toluene blend to a ⅓ solids solution. The remainder of solvents added is isopropanol only. Isopropanol is used in a quantity to yield a final ratio of toluene to isopropanol in the coating solution of about 1:46.125.

In the removal of letters imprinted by the impact of a type font with any of the above formulated transfer mediums, it has been found that there are several adhesive tapes which are particularly useful. Adhesive tapes designated by the designation Y9272 and 853 and 351 are available from the Minnesota Mining and Manufacturing Company. A product designated by product #7321 is available from Borden Company and adhesive tape designated by a product #440 is available from Nashua Corporation, Nashua, N.H.

In the formulation and production of the above ribbons, the coating weight, humidity, ink temperature, and drying temperatures should all be maintained in accordance with Example 1.

While the invention has been particularly described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that the foregoing and other changes in form and details may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. An adhesively eradicable transfer medium comprising a thin flexible substrate and a solvent coated ink transfer layer for complete release transfer to an imaging surface, said complete transfer ink transfer layer comprising;

from about 20 to 55 weight percent of a hard non-waxy resin;

from about 20 to 65 weight percent of a modifier to embrittle and harden said resin and make said resin less adherent for said flexible substrate;

said modifier comprising a mixture of about 20 to 65 weight percent of a tensile strength reducing material for reducing the tensile strength of said resin and from 0 to 45% of an adherence reducing release agent, wherein said tensile strength reducing material is a white mineral oil, and said release agent is selected from the group consisting of mixed octyl esters of fatty acids, isopropyl palmitate, butyl stearate, and mixtures thereof, and;

from about 5 to 30 weight percent of a coloring matter selected from the group consisting of pigments and organic coloring matter which are insoluble in the constituents of the ink layer.

2. The transfer medium of Claim **1** wherein said resin is a polyamide.

3. The transfer medium of Claim **1** wherein said coloring matter is carbon black.

4. An adhesively eradicable typewriter ribbon comprised of a thin film substrate;

an ink layer of the complete transfer type;

said ink layer comprised of an ink having from about 25 to 35 percent of a polyamide resin,

from about 15 to 30 percent of a white mineral oil;

from about 15 to 25 percent of mixed octyl esters of fatty acids;

and from about 25 to 35 percent coloring material selected from the group consisting of pigments and organic coloring matter insoluble in the other ink constituents.

5. A transfer medium comprised of a substrate and a completely transferable ink layer for transfer to an imaging surface, said completely transferable ink layer comprised of a hard, film forming non-waxy resin, a pigment, and a resin film tensile strength reducing material, said material comprising an oil selected from the group consisting of white mineral oil and coconut oil wherein said pigment is dispersed throughout said resin and said resin is mixed with said oil and the tensile strength is reduced, whereby said ink resin is easily fractured under impact and deposited on an imaging surface and remains hard enough to be removed by adhesive engagement of the imaged ink layer material deposited on said imaging surface, by an adhesive material.

6. The transfer medium of Claim **5** further comprising an adhesion reducing agent, said agent being a fatty acid ester, whereby the adherence of said ink layer for said substrate is reduced.

7. The transfer medium of Claim **6** wherein said adhesion reducing agent is a mixture of octyl esters of fatty acids.

8. The transfer medium of Claim **6** wherein said fatty acid esters are isopropyl palmitate and butyl stearate.

9. The method of making an adhesively correctable transfer medium of the complete transfer type, comprising the steps of,

coating a thin flexible substrate with a complete transfer ink layer which is the solid dry residue of a solvent solution and dispersion of a hard, film forming, non-waxy resin, a modifying material for hardening and embrittling said resin comprising an oil selected from the group consisting of white mineral oil and coconut oil, and coloring material;

and drying said solvent from said solution and dispersion, at a temperature of from about 100° F. to 140° F. in an atmosphere having from about .006 to .009 pounds of water per pound of dry air.

10. The method of Claim **9** further comprising the step of adding to said solution and dispersion an adherence reducing release agent comprising at least one fatty acid ester; and

wherein said resin is a polyamide, and wherein said coloring material is selected from the group consisting of pigments and coloring matter which are insoluble in the other constituents of said transfer medium.

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