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SPONGEOUS SUPPORTED TRANSFER MEDIUM AND POLYCARBONATE EMBODIMENT

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ABSTRACT OF THE DISCLOSURE

A transfer medium is provided by a coating process whereby the transfer layer is a resin, for example a polycarbonate, having voids or discontinuities which hold an imaging material in the pores in the manner of a sponge. An ink depleted surface is formed at the writing surface by the correct control of the solubilities of the resin and imaging material components in the coating layer dispersant. When the dispersant is evaporated a crust of pure resin is formed at the writing surface which is substantially free of imaging material producing a transfer medium, for example carbon paper, having clean handling properties.

DISCLOSURE OF THE INVENTION

This invention relates to the technology of synthetic plastics and of the carrying of marking materials within such synthetic plastics. A primary application for this invention is in the fashioning of transfer mediums such as improved materials functioning as carbon papers.

A unitary, spongeous transfer medium fashioned from synthetic resins is taught in patent application Ser. No. 171,188, filed Feb. 5, 1962, now abandoned and continuation-in-part application Ser. No. 536,557 filed Mar. 9, 1966, both entitled "Transfer Medium and Method for Making Same," invented by the same Hugh T. Findlay who is an inventor herein and Mr. Kenneth H. Froman, and assigned to the assignee of this invention. The primary benefits of such a unitary structure is in the thin transfer medium obtained. Imagining quality is greatly enhanced by thinness of the medium, and, of course, the cost of fabricating such a medium is reduced in proportion to the smaller amount of materials used. A thin transfer medium greatly enhances available storage capacities since more useful material can be stored in the same space.

Spongeous transfer layers are well understood in many aspects in the prior art, and there is no physical prohibition to supporting such spongeous transfer layers by coating them on preformed substrates such as thin sheets of polyethylene glycol terephthalate or polyethylene. The substrate may be manufactured and rolled into a bulk roll prior to the process which forms the finished transfer medium. The substrate may be fed from the bulk roll during the process. The substrate is unrolled into coating equipment and the spongeous transfer medium in a dispersed form is coated on top of the substrate. Shortly thereafter, the transfer layer is hardened by driving off a solvent or otherwise curing the spongeous layer. The transfer medium consists of the transfer layer and the support layer and is manufactured as just described. It may be cut and manipulated into typewriter ribbons or sheets for use as carbon paper.

To permit adequate handling of the preformed substrate during processing such preformed substrates must be relatively thick. Since print image quality and storage capacities both improve with the diminishing thickness of that transfer medium, use of the preformed substrate is therefore contraindicated. A supported transfer medium in which the support layer need not be handled separately is thus inherently desirable in this respect, since it is available to form such a transfer medium with a much thinner support layer. In the above referenced abandoned patent application Ser. No. 171,188, a transfer medium is taught in which no separate substrate layer is applied. That patent application also teaches a supported, spongeous transfer medium in which a transfer layer is fabricated and in which a supporting layer is then coated on top of the transfer layer.

This patent application is concerned with a transfer medium of the general kind in which a supporting layer is included essentially in addition to the spongeous transfer layer. It has been found that the supporting layer is often highly desirable to provide increased strength to the transfer medium for handling during normal operations. Also, the supporting layer effectively seals the back of the transfer medium so that imaging material cannot be expressed from the back. As will be immediately recognized, this sealing is very important when the transfer medium is to be used as a carbon paper.

A significant design criterion in any transfer medium is cleanliness during normal handling. Transfer mediums of the various kinds are, of course, frequently handled during use. Typewriter ribbons, for example, are handled when they are threaded into or otherwise inserted in the ribbon feed mechanisms of the typewriter. Carbon papers are handled even more frequently, especially as they are interleaved between various pages of print receiving paper or other material. During storage, it is also highly desirable that imaging material does not sweat out and mar adjoining sheets of transfer medium or other material.

It is an object of this invention to provide a potentially very thin transfer medium which is significantly increased in cleanliness to normal handling.

It is a further object of this invention to provide a potentially very thin transfer medium which does not sweat or exude ink during normal storage or handling.

In accordance with this invention, the migration of ink layer and resinous layer, which migration is taught for the first time in the above referenced abandoned Ser. No. 171,188, is utilized in a manner carefully controlled to obtain a cleaner transfer medium. In its broadest aspects, this invention contemplates the control of migration by selection of materials to provide a migration of a relatively ink free layer away from the support layer. It has been found that the materials can be adjusted or selected by experiment so that migration toward or away from the temporary substrate can be selected by selection of materials.

It has been found that the material most soluble in the solvent tends to follow that solvent as it is driven from the solution. Generally, the most useful way to disperse a resin is to solvate it. During processing the solvent can only escape in large amounts on the side of any laminates away from the temporary substrate upon which laminates are deposited during the fabrication process. In its more preferred aspects, therefore, a complete new sequence of steps is followed. An ink free resinous layer is first layed upon a temporary substrate. Then a layer of dispersed imaging material and resin is deposited upon the ink free layer. The migration within the ink containing layer is controlled by proper selection of the compounds so that only a slight tendency exists for the pure resin to migrate away from the temporary substrate during exhaustion of the dispersing medium occurs. This sequence of steps results in a slight crust or significantly ink depleted surface being obtained at the side of the transfer layer formed away from the temporary support. This ink depleted surface prevents migration of ink during normal handling and storage, but it has been found that the ink expresses from the spongeous resin onto a paper or print receiving surface in a manner fully adequate to give fine write quality.

In its more preferred aspects, this invention distinguishes over the prior art radically in the sequence of steps followed. It distinguishes in substance over the prior art in the control of migration so as to obtain an ink depleted outer layer to thereby achieve a clean transfer medium. In the prior art it was apparently assumed that the ink expressing side of the resinous sponge should contact the temporary substrate so that a very smooth surface is provided on the side of the transfer medium which will ultimately contact the print receiving paper and transmit an image to it. It has been determined, however, in accordance with this invention that the smooth surface thereby obtained can be dispensed with. Although the side of this ribbon away from the temporary substrate in accordance with this invention is the printing side, tests have shown that fine print quality is nonetheless obtained.

Applicants have on file in the United States Patent Office application Ser. No. 428,892, filed Jan. 25, 1965, entitled "Spongeous Transfer Ribbon" and assigned to the assignee of this invention. That invention shows a transfer layer solution containing 450 grams of nylon, and 450 grams of graphite, all dissolved and dispersed in 3,680 grams of denatured ethyl alcohol. The invention in that patent application, however, differs basically from the approach herein. That invention is primarily for use as a typewriter ribbon, and as such was compounded without special regard to the clean handling characteristics of the product. Thus, although about the same amount of solvent was provided, the solubilities of the materials are significantly different, so the surface facing the temporary substrate during the production of the ribbon in our Ser. No. 428,892 is greatly increased in quantity of ink as a result of the migration of the resin to the side away from the temporary substrate. In the instant invention the solubility factors are controlled so that the migration of the material to an ink rich layer and a resinous layer is small but nonetheless significant. The ink depleted surface is the printing surface of the final product, thereby presenting a crust which holds the imaging material during normal handling and storage and keeps the product clean to the touch. During use, however, it has been found that the ink expresses well and gives fine print quality even though the ink, of course, must be forced through the crust during printing from the transfer medium.

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

In accordance with the preferred aspects of this invention, the ink mixture is first compounded. The ink mixture may be compounded at any time and stored indefinitely. The ink mixture is the imaging material which will be mixed with a solvated, resinous material and which will be left primarily in fractures or voids within the resin material after the product is made. The ink mixture formula is as follows:

INK MIXTURE

Material:	Percent by weight
Bicrome black No. 7623 (Product of Brooklyn Color Works)	25
Sorbitan monopalmitate (Glycomal P—Product of Glyco Products Co.)	15
Naphthenic mineral oil No. 40 (K—Pale No. 40—Product of Standard Oil Co. of Kentucky)	60

In the above formula the bicrome black has been selected by a process of trial and error for its excellent imaging qualities. It has a blue tone which gives a good, black appearing print in actual use. It has also been found that it issues through the pores of the spongeous resin

more readily than other pigments, at least in the environment herein described. The sorbitan monopalmitate is a solid, wax-like substance. It serves as a wetting agent in this embodiment so that the pigment is more readily controlled by the physical movements of the vehicle. The mineral oil, of course, is the vehicle for the pigment. Selection of this mineral oil, as will be made clear below, is uniquely important with regard to this invention. Varying amounts and directions of migration of a resin rich layer toward one side and an ink rich layer toward another are obtained depending upon the chemical nature of the vehicle used. Since in accordance with this invention it is desired to obtain a very moderate amount of this layer dispersion, the specific mineral oil selected was chosen with this in mind.

The ink dispersion is obtained by use of a 5-inch by 12-inch three-roll dispersion mill manufactured by the J. H. Day Co., Cincinnati, Ohio. In this device the mixtures are pored to the feed roll and they exit from the take-off roll. To compound the ink mixture the three items in that mixture are simply mixed together. They are first processed with two passes through the three-roll dispersion mill. On these two passes the input roll is at 50 pounds per square inch pressure and the output roll is at 100 pounds per square inch pressure. The mixing of the ink mixture is completed with three further passes. During these passes the input roll is at 150 p.s.i. and the output roll is at 200 p.s.i. When this is properly performed, the ink composition is permanently mixed and will not settle for an indefinite period of time.

At the time of the production of a transfer medium in accordance with this invention, a transfer layer mixture is compounded. The transfer layer mixture is later applied as will be described. The transfer layer solution consists of the following parts:

TRANSFER LAYER MIXTURE

Material:		Proportions (by weight)
Polycarbonate (Lexan No. 105—Product of General Electric Co.)	parts dry weight	2
Diatomaceous earth (Superfoss—Product of Johns Manville Co.)	parts	1
Ink composition (above formula)	do	3

The Lexan No. 105 is made up as a 10% solution in methylene chloride. Two parts dry weight of polycarbonate in the above formula is thus supplemented with a further amount of 18 parts methylene chloride. That methylene chloride is the solvent and dispersant for the transfer layer solution. The transfer layer mixture is completely dispersed, that is: the polycarbonate and the vehicles are dissolved and the other materials are suspended indefinitely, simply by mixing all of the materials of the transfer layer solution for a short time at room temperature in a Cowles dissolver. The dispersant will be driven off after application of the transfer layer, leaving behind the transfer layer of resin holding the ink in a manner comparable to that of a sponge.

In the transfer layer solution, polycarbonate is selected because it is a tough resin which will therefore resist the cutting action of an impacting type die adequately. The diatomaceous earth is basically a finely divided, chemically inert filler for the polycarbonate which is necessary to give added strength to the product and also to influence the extrusion of imaging material from within the pores of the product. Without such a filler parts of the imaging material tend to be expressed too vigorous, and often the pigment tends to be retained. The ink, of course, is basically the imaging material. As in the prior art, the ink is essentially incompatible with the resin. However, it was important that the vehicle for the ink was chosen with regard to the gist of this invention. The naphthenic mineral oil used is not quite, but almost as soluble in the methylene chloride as the polycarbonate. This is important to the mechanism whereby a pure resinous layer tends to migrate in one direction and an ink rich layer tends to migrate in another during the extraction of the solvent. Migration is also reduced by reducing the amount of dispersant (methylene chloride) used, and this was a factor in formulating this preferred embodiment. The mineral oil was selected in accordance with this theory but primarily by experiment to obtain a composition in which the amount of migration is significant but not great. As will be made clearer further below, this type of migration will provide the clean transfer medium in accordance with this invention.

THE PROCESS

The structures to apply the mixtures and drive off the solvents to produce the transfer medium are quite similar to those described in the above referenced application Ser. No. 171,188. However, in accordance with this invention a pure layer of a solution of the lexan polycarbonate in 10% by weight methylene chloride is first applied. The amount applied can be controlled so that the dry thickness is within one quarter mil (0.00025 inch) thick or to one mil (0.001 inch) thick or greater. The one mil thick system gives an extremely strong system which is resistant to the impact of a type die. On the other hand, the ¼ mil thickness, by virtue of its thinner dimension, affords a very good write quality. This pure polycarbonate mixture is placed in the roll coater basin as shown in the referenced application Ser. No. 171,188 in which an applicator roll of a reverse roll coating applicator is situated. A temporary substrate made of polyethylene glycol terephthalate is played out through the roll coater while the applicator roll applies the supporting layer to the temporary substrate. The mechanism leads to a drying oven with appropriate exhaust fans.

A complete pass is conducted in which a layer of pure polycarbonate solution is applied to the polyethylene glycol terephthalate film and dried. The polyethylene glycol terephthalate film with the dried layer is collected on a roll at the terminal location of the dryer. The roll of polyethylene glycol terephthalate with the dried and therefore solid polycarbonate on it is placed in the playoff position of the solvent coating apparatus. The basin of the coating apparatus is then filled with the transfer layer mixture above described. Then the entire operation is repeated with the applicator roller of the coating applicator this time applying the transfer layer. The polycarbonate is applied to give a dry thickness preferably between one half mil (0.0005 inch) and one mil thick. The one-half mil thickness affords a smaller reservoir of ink for repeated use of the transfer medium, but the decreased thickness provided improved write quality. The one mil thickness affords longer life at the cost of write quality.

The polyethylene glycol terephthalate with the substrate and the transfer layer coated upon it feeds into the evaporating ovens where the fabrication is completed by the expulsion of solvent from the transfer layer. When this step is complete, a roll of polyethylene glycol terephthalate exists as a temporary substrate containing bulk quantities of the completed transfer medium. The transfer medium can be stripped from the substrate and cut into carbon papers or slit into typewriter ribbons.

THE PRODUCT

The final product contains two layers, the transfer layer and the support layer. The transfer layer has two opposite sides, one of which is bonded to the support layer while the second side is unobstructed. In use a type die impacts the support layer to thereby express ink mixture from the unobstructed side of the transfer layer onto paper or other receptive materials. The ink exists normally in the pores of the transfer layer where it is held as globules.

Due to judicious selection of materials in accordance with this invention the globules of ink have migrated slightly toward the support layer and pure polycarbonate

has migrated slightly toward the unobstructed side. This has been verified by microscopic examination. A very thin and apparently almost continuous outer layer of pure resin is formed. Thus, a minute crust is formed or at least an area in which the amount of voids with relation to resin is significantly reduced. It has been found that this functions to cause the unitary transfer medium to handle and store without losing ink or imaging material to any appreciable extent. The transfer medium is therefore very clean. Nevertheless, during the heavy impact of a type die in normal typing, ink is expressed very well through the crust or outer layer, and the imaging quality is therefore of fine quality. It is believed that a number of fractures or ink containing voids exist in the crust sufficient to provide channels for the ink under the heavy pressure of a type die.

DESIGN CRITERION OF PRODUCT

Although it has not been possible at this time to usefully describe quantitatively the specific magnitudes of the dispersion of ink rich and ink depleted layers, the product obtained is nonetheless well understood. That product appears to be quite novel, and, as such, the product establishes a design criterion within this technology. In addition to the relatively ink free layer through which the entrapped materials are expressed, the product is characterized by a continuous phase containing a synthetic polymer as a major structural component. (It is also often desirable, of course, that the continuous phase also contain a filler.) The product is further characterized by having a total of components basically making up the discontinuous phase expressable under pressure which is about equal by weight or of the same order of magnitude by weight or less by weight than the total quantity of the components basically making up the continuous phase.

Prior art supported transfer mediums have consistently used considerably more of the discontinuous phase than of the continuous phase when the continuous phase comprised a synthetic polymer. Synthetic polymers are highly desirable for use in this technology since they are resistant to environmental factors under normal handling conditions and are inexpensive. The prior art, however, apparently did not understand the dispersion of ink free and ink rich layers which could be controlled as herein taught Although such dispersions may have occurred occasionally in the prior art, they were not properly compensated in the design of the product. As a result, the prior art uniformly teaches supported transfer layers of the general kind herein described (i.e., possible dispersion of layers to provide a crust for clean handling and synthetic polymer matrix material) which, in view of this invention, can now be recognized as being overloaded with the discontinuous, expressable phase.

Such overloading was probably found to be necessary by empirical test in order that the end product should be capable of expressing sufficient ink. Doubtless, however, in view of the teachings of this patent specification, the art will adjust its techniques to obtain the controlled dispersion which provides the clean handling product. It would be possible, for example, to extract the solvent from both sides of a fluid sheet in proportions which control the layer dispersion obtained.

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

We claim:

1. A process for making a supported, spongeous transfer medium comprising:

coating on a temporary substrate a first layer of support material contained in a volatile dispersant and a second layer of a dispersed mixture comprising volatile dispersant, resin, and ink, said ink being at least substantially imcompatible with said resin, the dispersed resin and ink mixture being selected so that a migration of said resin occurs relative to said ink during expulsion of the dispersant from said mixture to form a substantially ink free, thin resin crust on the side opposite said temporary substrate, and

expelling said dispersants, and then stripping said medium from said temporary substrate.

2. The process as in claim **1** in which said layer of support material is coated on said temporary substrate and then said resin and ink mixture is coated.

3. The process as in claim **2** in which the dispersant for said support material is first expelled and then said resin and ink is coated.

4. The process as in claim **1** wherein the resin of said resin and ink mixture is dispersed by being solvated in a solvent for said resin in said resin and ink mixture.

5. The process as in claim **2** wherein said resin in said resin and ink mixture is dispersed by being solvated by a solvent for said resin in said resin and ink mixture.

6. The process as in claim **3** wherein the resin in said ink mixture is dispersed by being solvated by solvent for said resin in said resin and ink mixture.

7. The process as in claim **4** wherein said ink is in a vehicle which is slightly less soluble in said solvent than said resin.

8. The process as in claim **5** wherein said ink is in a vehicle which is slightly less soluble in said solvent than said resin.

9. The process as in claim **6** wherein said ink is in a vehicle which is slightly less soluble in said solvent than said resin.

10. The process as in claim **2** in which said resin in said resin and ink mixture is a polycarbonate resin.

11. The process as in claim **10** in which said polycarbonate resin is dispersed by being solvated in methylene chloride and said ink is in a vehicle of naphthenic mineral oil.

12. The process as in claim **11** in which said resin is about two parts by weight and in which about one part by weight of a finely divided, chemically inert filler is also in said resin and ink mixture and in which said methylene chloride is less than 95% by weight of combined weight of said methylene chloride and said polycarbonate resin.

13. The process of forming on a support, a layer of a resin containing an imaging material in its pores, said material being capable of being expressed under pressure from said layer, comprising the steps of:

coating a layer of a dispersed mixture comprising volatile dispersant, imaging material, and resin, said imaging material being at least substantially incompatible with said resin, the dispersed imaging material and resin being selected so that said resin is slightly more soluble in said dispersant than said imaging material such that a migration of said resin occurs relative to said imaging material during the expulsion of said dispersant from said mixture to form a spongeous transfer medium having a substantially ink free slight resin crust on the side opposite said support, and expelling said dispersant.

14. The process as in claim **13** wherein said dispersant is less than 95% by weight of combined weight of said dispersant and said resin.

15. The process as in claim **14** wherein said resin is polycarbonate.

16. The process as in claim **15** wherein said resin is about 10% by weight of the combined weight of said dispersant and said resin.

17. A spongeous transfer medium in which a transfer layer comprising a discontinuous ink phase is held in a continuous resin phase containing a synthetic polymer as a major structural component and in which said discontinuous ink phase is expressable under pressure and in which said transfer layer is bonded on a support layer characterized by said discontinuous ink phase being relatively depleted on the side of said transfer layer away from said support layer such that the transfer surface comprises a substantially ink free thin resin crust and further characterized by the material basically making up the discontinuous ink phase being less than or equal to about the same order of magnitude by weight as the material basically making up said continuous resin phase.

18. The product as in claim **17** in which said material basically making up said discontinuous ink phase is about the same order of magnitude by weight as said material basically making up said continuous resin phase.

19. The product as in claim **17** in which said material basically making up said discontinuous ink phase is about equal or less in weight to said material basically making up said continuous resin phase.

20. The product as in claim **19** in which said material basically making up said discontinuous ink phase is about equal in weight to said material basically making up said continuous resin phase.

21. The product as in claim **20** in which said synthetic polymer is a polycarbonate.

22. The product as in claim **17** in which said continuous resin phase contains a finely divided, chemically inert filler.

23. The product as in claim **18** in which said continuous resin phase contains a finely divided, chemically inert filler.

24. The product as in claim **19** in which said continuous resin phase contains a finely divided, chemically inert filler.

25. The product as in claim **20** in which said continuous resin phase contains a finely divided chemically inert filler.

26. The product as in claim **21** in which said continuous resin phase contains a finely divided, chemically inert filler.

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