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## PRINTING INK, PROCESS OF PRINTING, AND ARTICLE FOR USE THEREWITH

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This invention relates to a method for producing typewritten characters or letters on non-porous, synthetic organic materials of certain types, and to a typewriter ribbon and ink suitable for use in this method.

One of the objects of my invention is to provide a method and means for impressing characters on organic plastic materials of the type of cellulose acetate, by means of a typewriter.

A further object of the invention is to provide a method for typing on transparent organic sheet materials, characters of such sharpness of definition and opacity to light, that they may be used in projection apparatus for throwing printed matter on a screen or other light intercepting surface.

A still further object of the invention is to provide a typewriter ribbon so treated that it will not dry out or set on standing at room temperatures for long periods, but which will imprint characters upon non-porous synthetic organic materials of selected characteristics, which will dry very rapidly when typed, and which will be clear cut, intense and legible at magnifications of the order of 5 to 10 times when projected onto a screen or other surface.

For many purposes, in furnishing news or other information such as stock quotations and the like, to assembled crowds, it has been customary to project this information onto a screen, or other light intercepting surface, using transparent, typed or printed sheets through which the light passes except where obscured by the printed characters.

In preparing such printed surfaces for projection, it has been the practice in the past to type on glassine, i. e., a transparent paper material, with ordinary or specially prepared typewriter ribbons. The results thus obtained have never been entirely satisfactory, as the glassine was not completely transparent, and moreover was extremely brittle and subject to breaking in the projector mechanism and upon handling. Furthermore, such practices would not obtain a clean cut, sharp print which would be sufficiently intense and opaque, and which would set immediately upon typing. The same objections obtained when regenerated cellulose material (Cellophane) was used.

The recent introduction of television has increased the demand for a clean cut, sharp and opaque typed print on transparent material which can quickly and easily be produced by means of typing in an ordinary typewriter. In television broadcasting, actors are not permitted to hold and read from a typed script as is the present practice in ordinary broadcasting. By the use of the present invention the script may be typed on transparent material and projected onto a screen outside the range of the picture being broadcast, but within the line of vision of the television actors. In typing upon paper, or the like using an ordinary typewriter ribbon, the ribbon ink material must not only remain sufficiently non-solid or fluent at room temperatures under the ordinary conditions of use, but it must transfer an impression which will dry or set so as to be smudge proof almost immediately on transference. This can be accomplished readily enough for printing on paper and other relatively absorbent materials, by using extremely high boiling solvents such as glycerin, which are practically non-volatile even at elevated temperatures, and which upon typing penetrate into the paper leaving the coloring material on the surface, and partly imbedded in the fibers of the sheet by the impact of the type element.

However, on such non-porous materials as glassine, regenerated cellulose and other transparent, non-absorbent sheets, their non-absorbency has practically prevented the obtaining of dry, smudge proof characters of sharp definition suitable for use in projection. As the solvent could not penetrate it tended readily to smear out beyond the outline of the printed characters upon the impact of the type, and would readily smear on contact. Also such prints when obtained are of low intensity containing relatively low concentrations of opaque coloring materials. In typewriter ribbon ink the percentage of color, including both pigment and dye, ranges from concentrations of around 5% or below, to a few containing as high as 20% coloring matter. This higher figure represents about the maximum percentage of coloring matter which is incorporated into a typewriter ribbon ink material, even in cases where no binder or thickening material is used. Besides being unsatisfactory in failing to produce a clear sharp print, such materials further fail to provide enough opacity for the projection desired by me.

I have now discovered that these difficulties, of lack of sharpness of definition and lack of opacity and intensity of the print, can be overcome in the practice of my invention by using a transparent sheet material, which is soluble in, or softened by, the vehicle used for the ink material to be transferred thereto. Thus by the use of certain organic solvents and certain trans-

parent sheet material each selected with respect to the other and having coordinated characteristics of intermaterial responsiveness I can prepare a typewriter ribbon impregnating compound whose vehicle has the required sheet solubility, and also possesses the necessary evaporation and other characteristics for setting. I can thus produce a transparent typed material which will dry almost immediately upon typing and which will be smudge proof in use, and moreover will have the clear definition necessary for projection by strong light sources on screens and the like.

I have found that only those transparent organic materials may be used for the sheet which are soluble in, or are softened by solvents which combine the necessary evaporation rates and the mutual solvent power for my purpose. Examples of such sheets are cellulose acetate, vinylite, (a vinyl acetate-vinyl chloride polymer), and lacquered Cellophane. Regenerated cellulose and glassine, and the like which are not soluble are not suitable, unless coated or surfaced with a transparent material or lacquer of the referred to character.

In preparing the typewriter ribbon for this purpose, I make a paste comprising a vehicle and coloring matter in which the ingredients are all selected to conform to critical narrow requirements of mutual solvent properties, evaporation rate and acidity, and in which I am able to incorporate high intensity, opaque coloring materials in extraordinarily high proportions—far greater than has previously been considered the maximum possible quantity.

As the vehicle, I use a solvent or softening agent for the particular material on which the typing is carried out. This allows penetration or bonding or solution-admixture of the solvent into and upon the base to cause the ink to dry or set with sufficient rapidity, and also serves to utilize a portion of the printed surface as a binder material for the color, and to prevent the spreading and smudging so often present in typewriter ribbon pastes especially when attempt is made to use on non-absorbent surfaces. The solvent must have a high enough boiling point so that the ribbon will not dry out on standing at room temperatures, under the conditions of use. Furthermore, its boiling point must not be so high that it will completely resist evaporation when typed, as such a solvent will deposit a film which will smudge after typing.

The vehicle, besides being a solvent or softening agent for the basic sheet material, is also an exceptionally good solvent for the intense, oil soluble dye materials so as to produce an opaque print which will obscure the strong light of the projecting source.

I have found that the higher boiling solvents, suitable from the point of view of non-drying, are in most cases too low in solvent power either for the dye material or the transparent sheet material; and, in general, solvent power decreases with increase in boiling point of the material selected. This solvent power must be present in the heretofore unattainable amounts, sufficiently high amounts for the intense dyes such as methyl violet base being needed to impart the required opacity. The effort to use solid pigments in substantial quantity to increase opacity creates a print which is fuzzy and indistinct in outline, especially noticeable when the letters are magnified in projection.

Because the maximum quantity of coloring material was limited in the case of pigments by the thickening action and fuzzy prints caused thereby, and in the case of dyes by their limited solubility in the materials used, substantial practical operating limitations and objections were inherent in attempted uses as described. I have now discovered that a solvent may be used which is initially a relatively good solvent for the intense dye base, and which is acidified, slightly, so that it has a pH value as measured by the Beckman pH meter using a glass electrode with a calomel reference electrode of around 3.03 or below, and that with such the amount of the dye material which can be effectively incorporated is nearly doubled. Although many commercially available solvents are acid in pH I have discovered the surprising fact that such usual and incidental acidity is not enough, but it is only after the pH is reduced to the pH around the figure named (i. e. about 3.03), or below, that the necessarily large increase in dissolving power is attained. For example, a sample of commercial carbitol acetate as received when tested had a pH of 3.12 and yet was found entirely unsatisfactory in the high solubility characteristics, being capable of dissolving only about 15% of methyl violet base, a quantity in the neighborhood of the prior art maximum quantities. But when sufficient acid was added to reduce the pH to 3.03 the solubility suddenly increased enormously, so that it was then possible to incorporate nearly 40% of the dye. Greater additions of acid increased the solvent power and permitted the incorporation of additional amounts of the dye, but such additions increased the viscosity until finally impairing the penetration characteristics needed for the ink material to penetrate and soak into the ribbon. Added solvent power attending added acidity thus should be so limited that the viscosity, impregnating and other characteristics required in the ribbon impregnating compound will still be present. Concentrations of about 30% or more of dye in my paste produce prints which are quite satisfactory from the point of view of opacity. However, I prefer to use concentrations between about 35 and 40% to give a satisfactory viscosity range, together with the desired opacity. Such die additions, to produce the desired color intensity, affect the viscosity which increases as the percentage of dye in the solvent increases, and I have found that in such high concentrations no binder can be used because of the limitations imposed by the working viscosity required. Without such binders dye solutions in the solvents which I employ, having concentrations sufficiently high to give the intensity and opacity necessary to fulfill the requirements of my invention, have viscosities so high as to be at about the upper limit of good working qualities; and any addition of binder raises the viscosity still further and makes the ink too viscous for use. Thus inks containing binder, and within the working limits of a typewriter ribbon, can be produced only by a sacrifice in the dye used. This, however, renders the resulting prints less effective for my purposes, and even too light for projection purposes. In my ink a binder is not necessary as the print when applied to the soluble base dissolves sufficient of the binding material of the base to insure strong adherence and binding of the material of the print to the base; and I have found the surprising result that by the use of my invention I can make a legible print which is adequately displayed by reflected light as well as by transmitted light, the shadow cast in the latter event being satisfactory for projection.

For imparting a desired body to my paste, I may include a small quantity of an inert filler

material in finely divided form. This filler or other solid material seems to serve the purpose of preventing the squeezing out of the ink at the edges of the impression by forming small solid spacers or obstacles effective between the type mechanism and the sheet to be printed to prevent the type impact from squeezing out all the ink and leaving a blank. It is evident that only a small portion of the filler is required, sufficient merely for holding the type mechanism and printing surface the necessary short distance apart to insure the deposition of an adequate film. This filler can conveniently be carbon black, or any other finely divided solid which will give the desired thickening or non-squeezing effect to the paste. The amount of the filler material added is not controlled by considerations of color material and the small quantities which I would ordinarily use are insufficient to materially change the intensity of the projected shadow. As stated, such filler is not used for pigmenting purposes, although it may contribute in some slight measure to this effect.

A paste found suitable for impregnating the typewriter ribbon of my invention is given below in parts by weight:

| | |
|---|---|
| Carbitol acetate, pH 3.03 | 58.8 |
| Carbon black | 3.0 |
| Methyl violet base | 38.2 |
| | 100.0 |

This paste has a viscosity of 900 centipoises at 21.8° C.

Carbitol acetate, (diethylene glycol monoethyl ether acetate), with a boiling point of 218° C., is a very powerful solvent for cellulose acetate and also for vinylite and other synthetic resins. Moreover, when acidified as described, such solvent power is not impaired and also it becomes an excellent solvent for such intense, oil soluble dye bases as methyl violet base.

I have found that most commercially available solvents when made as outlined to be within the critical pH range will not have these combined solubility characteristics and to produce them in a single solvent is extremely rare, and even if so the solvents which do exhibit these combined features are most of them unsuitable for my typewriter ribbon for other reasons. For example, diacetone alcohol, boiling at 164° C., is an excellent solvent for both the strong dye bases and for cellulose derivatives and other transparent plastics, but it is unsuitable for my purposes because of its rapid evaporation rate (low boiling point), which causes a typewriter ribbon impregnated with a solution containing it, to dry out too rapidly for any practical purposes, in fact, mere exposure of the freshly impregnated ribbon for the period of unrolling necessary in typing, drys the ribbon so quickly that even a single satisfactory typing may not be obtained.

Butyl carbitol acetate, boiling at 245° C., while an excellent solvent for the transparent base materials used, is unsuitable at room temperatures because of its high boiling point. While it may penetrate to the necessary extent by virtue of its solvent power for the base, and although only very slight evaporation is required in practice, this solvent does not possess even that slight degree of evaporation at room temperatures necessary for a smudge proof impression. I have found that only solvents as described and boiling within a very narrow range of boiling points can be used. I have found boiling points between about 200° C. and 225° C., to be satisfactory with solvents of the solvent power and acidity of my invention; and, other satisfactory dyes in addition to the methyl violet previously mentioned, are Victoria blue base, nigrosine base and induline base.

I prepare my paste by first acidifying the solvent to a pH of about 3.03, with any suitable organic acid, for example acetic, then dissolving the dye in the solvent. I then add any desired amount of pigment or other inert powder or filler and grind in any suitable mill such as a ball mill, three roller mill or the like, until adequate dispersion is obtained. The typewriter ribbon fabric is then impregnated with the paste, for example, by passing the ribbon through a bath of the mixture at suitable temperature, and gently squeezing off the excess between squeeze rollers or similar means. Or, the paste may be applied by a wick mechanism or other means.

When typings are made with this ribbon on transparent, non-porous sheets of such character as to be partially dissolved or softened by the solvent portion of the vehicle, clean cut, dense, opaque impressions are produce which yield dark, legible characters when subjected to projection on a screen by passing light through the transparent portion, even when such projection takes place at high magnifications.

The typewriter ribbon thus prepared will remain suitably moist and usable in a typewriter for reasonably long periods of use, but if the ribbons are to be stored or kept in stock for appreciable periods before use, they may be kept in air tight containers to retard even that small amount of evaporation which takes place at room temperatures. Also it may be used for printing on lacquered or synthetic resin coated paper, on plastics, on moisture proof Cellophane (a lacquered regenerated cellulose), and synthetic resins of the alkyd, urea-formaldehyde, vinyl and many other types of resins and other surfaces.

While the product herein described and the method of printing or typing with it constitute preferred embodiments of the invention it is to be understood that the invention is not limited to this precise process and product, and that changes may be made therein without departing from the scope of the invention as described and defined in the appended claims.

What is claimed is:

1. A typewriter ribbon of the character described, adapted to transfer sharply defined, opaque, non-smudging characters to a non-porous organic material having solubility characteristics coordinated with the character of the printing medium applied, comprising a web material impregnated with an opaque printing composition comprising a liquid, said liquid being of pH not to exceed about 3.03, and which is substantially non-evaporating at room temperatures and which has a boiling range between about 200° C. and 225° C. and which has a predetermined rate of penetrating or solvent action upon said organic material when applied thereto as delineated characters and has of the order of 30% of a dissolved, high intensity dye base, whereby rapid setting of the printed characters to a sharp, smudge-proof condition is effected.

2. A typewriter ribbon of the character described, adapted to transfer sharp, non-smudging characters to non-porous, transparent, organic materials having solubility characteristics coordinated with the character of the printing

medium applied, comprising a web material impregnated with a composition comprising a soluble dye base and a liquid, said liquid being of pH not to exceed about 3.03, and which is substantially non-evaporating at room temperatures and which has a boiling range between about 200° C. and 225° C. and which contains in excess of about 30% and not more than about 40% of said dye base dissolved therein, and which composition has a predetermined penetrating or dissolving action upon the organic material when applied thereto as delineated characters, whereby rapid setting of the printed characters to sharply delineated, smudge-proof condition is effected.

3. A typewriter ribbon of the character described, adapted to transfer sharp, non-smudging characters to non-porous organic material having solubility characteristics coordinated with the character of the printing medium applied, comprising a ribbon-like fabric material impregnated with an opaque printing composition comprising in excess of about 30% and not more than about 40% of methyl violet dye base dissolved in a liquid said liquid being of pH not to exceed about 3.03 and which is substantially non-evaporating at room temperatures and has a boiling range between 200° C. and 225° C., and which composition has a predetermined rapid rate of penetrating or dissolving action upon the organic material when applied thereon as delineated characters, whereby rapid setting of the printed characters to a sharp, definitely opaque smudge-proof condition is effected.

4. A typewriter ribbon of the character described, adapted to transfer sharp, non-smudging characters to non-porous organic material having solubility characteristics coordinated with the character of the printing medium applied, comprising a ribbon-like fabric material impregnated with an opaque printing composition comprising methyl violet dye base in excess of 15% and not more than about 40% dissolved in a liquid, said liquid being of pH not to exceed about 3.03, and which is substantially non-evaporating at room temperatures and has a boiling range between 200° C. and 225° C., and which composition has a predetermined rapid rate of penetrating or dissolving action upon the organic material when applied thereon as delineated characters, whereby rapid setting of the printed characters to a sharp, smudge-proof condition is effected.

5. A typewriter ribbon of the character described, adapted to transfer sharp, non-smudging characters to a non-porous transparent organic material having solubility characteristics coordinated with the character of the printing medium applied, comprising a fabric material impregnated with a composition comprising carbitol acetate acidified to a pH of about 3.03, and methyl violet dye base in excess of about 30% and not more than about 40%.

6. An ink material of the character described, adapted to be printed upon a transparent base, comprising an organic solvent for the base having a boiling point between about 200° C. and 225° C., and a pH value not exceeding about 3.03; methyl violet dye base in quantities in excess of about 30% and not more than about 40%.

7. A typewriter ribbon of the character described, adapted to transfer sharp, non-smudging characters to a non-porous transparent organic material having solubility characteristics coordinated with the character of the printing medium applied, comprising a fabric material impregnated with a composition comprising carbitol acetate acidified to a pH of about 3.03, and methyl violet dye base in excess of 15% and not more than about 40%.

8. A typewriter ribbon of the character described, adapted to transfer sharp, non-smudging characters to a non-porous transparent organic material having solubility characteristics coordinated with the character of the printing medium applied, comprising a fabric material impregnated with a composition comprising carbitol acetate acidified to a pH of about 3.03, and methyl violet dye base in an amount of the order of 30%.

9. A typewriter ribbon of the character described, adapted to transfer sharp, non-smudging characters to transparent cellulose acetate sheeting, comprising a web material impregnated with substantially large quantities of an opaque printing composition comprising a liquid, said liquid being of pH not to exceed about 3.03, and being substantially non-evaporating at room temperatures and having a boiling range between about 200° C. and 225° C., and of the order of 30% of an intense dye base dissolved therein, and which composition has a predetermined rapid rate of penetrating or dissolving action on the cellulose acetate when printed thereon, whereby rapid setting of the printed characters to a sharp, smudge-proof condition is effected.

10. A typewriter ribbon of the character described, adapted to transfer sharp, non-smudging characters to transparent vinyl resin polymer sheeting, comprising a web material impregnated with substantially large quantities of an opaque printing composition comprising a liquid, said liquid being of pH not to exceed about 3.03 and being substantially non-evaporating at room temperatures and having a boiling range between 200° C. and 225° C., and of the order of 30% of an intense dye base dissolved therein, and which composition has a predetermined rapid rate of penetrating or dissolving action on the vinyl resin polymer sheeting when printed thereon, whereby rapid setting of the printed characters to a sharp, smudge-proof condition is effected.

11. An ink material of the character described, adapted to be printed upon a transparent base, comprising an organic solvent for the base having a boiling point between about 200° C. and 225° C., and a pH value not exceeding about 3.03; methyl violet dye base in quantity in excess of about 30% and not more than about 40%, and a small proportion of a finely divided inert solid material.

12. An ink material of the character described, adapted to be printed upon a transparent base, comprising an organic solvent for the base having a boiling point between about 200° C. and 225° C., and a pH value not exceeding about 3.03; methyl violet dye base in quantity in excess of about 30% and not more than about 40%, and a small proportion of carbon black.

13. An ink material of the character described, adapted to be printed upon a transparent base, comprising an organic solvent for the base having a boiling point between about 200° C. and 225° C., and a pH value not exceeding about 3.03, and a methyl violet dye base in quantities in excess of about 15% and not more than about 40%, and a small proportion of a finely divided inert solid material.

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