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TRANSFER INK

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1 Claim. (Cl. 106—23)

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My invention refers to transfer inks and products comprising such inks. In the following, the term "transfer ink" shall be used to denote inks as used primarily in connection with office machines such as typewriting, billing, bookkeeping, addressing, duplicating machines, stamping devices etc., as distinct from commercial printing machines, and applied to carbon paper, typewriter ribbons, inking pads and sheets, including screens in duplicating machines. These inks are considered to be of the non-drying type, as distinct from commercial printing inks of the drying type.

The term "ink" shall be used to denote the coloring composition used on the aforesaid transfer media regardless whether it is present as a surface coating, as a body impregnant or saturant. It comprises coloring matter intermixed with or dissolved in a vehicle. Likewise, the word "inked" shall have the meaning of coated, impregnated or saturated with coloring composition.

The term "carbon paper" shall be applied to any paper of that kind, capable of rendering copies, even if its coating does not contain carbon black, as a pigment.

The term "typewriter ribbon" shall refer not only to the narrow ribbons used in the conventional typewriter machines, but also to any inked textile or paper used in any other machine serving the purpose of producing typed or duplicated texts or markings.

It is frequently desirable to distinguish certain words, phrases or numerals by a different color. For example, it is customary to make bookkeeping entries in black and red colors, signifying credit and debit items, as the case may be. This need has been recognized by supplying, for example, typewriters with the well-known black and red ribbons and a mechanism by which either black or red typing can be applied to the original. However, this device is unable to transmit the color distinction to the carbon copies which are always black or in any other uniform color; hence, the copies are not entirely identical with the original and fail to reproduce certain important aspects thereof. The deficiency is so serious that special typewriters are made which have two sets of numerals, one in normal and the other in cursive script. By this means distinctions are transmitted to the copies but they are not as conspicuous as contrasting colors and it is impossible to duplicate all characters on a typewriter in this manner.

There are also certain office machines, such as

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billing machines, addressing machines, electric typewriters, typing machines using inking pads, stamping devices etc. which operate with the help of inked ribbons, sheets or pads; the mechanism of those machines does not permit the use of two colored inking devices, though, in many cases, the availability of more than one color would be most desirable.

It is an object of my invention to provide a carbon paper which, when used in the conventional way, permits the making of copies in more than one color. Another object is to provide typewriter ribbons, inked sheets or pads which, though inked in one uniform color, permit the making of typed or stamped texts or markings in more than one color. It is still another object to obtain these results by a simple treatment which can be executed without special skill. As a further object, the color variability is to reside completely in the ink of the transfer medium so that its imprint on any kind of available paper, fabric or other base may be made to change its color.

Conventional carbon paper ink is a mixture of oils, fats, waxes and/or resins serving as a vehicle for finely divided insoluble pigments and/or soluble dyestuffs. Record typewriter ribbon ink is similarly composed in principle, though with some changes regarding the composition and ratio of the basic ingredients. Thus, a black carbon paper or a black typewriter ribbon usually contains carbon black and a black dyestuff such as, e. g. a fat-soluble nigrosin base and/or other dyestuffs to neutralize eventual "undertones" and thus produce a pure, opaque black. The same principle is applied in carbon papers or ribbons of other colors, i. e., pigments and dyes of the same basic color are used in combination. While it is possible to make a carbon paper or a typewriter ribbon with an ink containing a dyestuff dissolved in the vehicle and no pigment or at least a relatively small amount of pigment, it is desirable to "fill" the ink with a considerable amount of pigment. This is especially true for ribbons. Not only do transfer inks containing no pigment or not enough thereof fail to meet the requirements of permanence of the typed or stamped texts and markings, including erasability with chemical ink eradicators, but they also exhibit a tendency to bleeding. A poorly "filled" ink is also the reason for unclear, inaccurately contoured typed copies since it spatters easily under heavy impact of the metal types, thus making the contours of their imprint hazy. A sufficient amount of pigment gives the ink enough

"body" to hold the colored mass together and to prevent it from spattering under impact. While a carbon paper ink can derive at least part of its "body" from the relatively high percentage of high melting wax which makes up part of the ink composition, a typewriter ribbon ink has to rely for "body" almost entirely on its sufficient pigment contents. Liquid inks at room temperature for ribbons, inking sheets or felt pads would definitely bleed and display an undesirable lack of opaqueness, unless they are heavily "filled" with pigment.

According to my invention, I incorporate into the ink vehicle a pigment or filler having one basic color, with the exception of black, and another pigment or colored filler having another basic color, including black, and different from the first; both pigments or fillers being insoluble in the vehicle; the second pigment being present in sufficient quantity either to produce, together with the first pigment, a substantially different ink color or to impose its own color by completely hiding, covering and suppressing that of the first pigment. This can be helped and improved by also adding a small amount of dyestuff or a combination of dyestuffs of the same basic color as the second pigment, or a dyestuff modifying the shade of the second pigment, but different from the color of the first pigment. In the following, the first pigment will be called the "hidden" pigment or filler and the second pigment will be called the "dominant" pigment or filler. The "dominant" pigment and the soluble dyestuffs so employed must be susceptible to the action of chemical agents capable of either destroying their tinctorial power or of changing their basic color, whereas the "hidden" pigment employed must be inert towards the same chemical agents and its color must not be affected thereby. In consequence, the chemical treatment of the typed or stamped text or copy makes the color of the "hidden" pigment appear, either as such or modified by the changed color of the "dominant" pigment and/or dyestuff, causing the treated passage to assume a contrasting color.

It is possible to suppress the color of the "hidden" pigment by incorporating into the vehicle only soluble dyestuffs of contrasting color, and no "dominant" pigment at all. But in this case the "hidden" pigment will constitute the total of fillers in the ink, a quantity which necessarily is limited, if the color of the "hidden" pigment is not supposed to show. On the other hand, as all the tinctorial power in the unreacted ink has to be contributed in such a case by the soluble dyestuff or dyestuffs alone, in order to suppress the tinctorial power of the "hidden" pigment, an excessive amount of soluble dyestuff is required. Both, the limited amount of filler and the excess of dyestuff may lead to the undesirable conditions as described in the foregoing, in particular, bleeding, lack of opacity and spattering; or, if these conditions can be compromised or reconciled to a certain extent, it will be at the expense of the purity of the color of the ink. The use of the "dominant" pigment makes it possible to produce an ink for carbon paper, typewriter ribbons and similar applications which embodies the best performance quality together with the additional feature of changeable color. Such products yield clear, clean colored, sharply contoured, steel type like imprints, writings or copies which do not bleed and are thoroughly opaque and permanent.

Depending on the type of the "dominant" pigment, the chemical agents that bring about the color change are oxidizing or pH controlling agents.

For example, a black transfer ink is obtained, if an inert red lake toner, such as an insoluble metal salt of a red dye is used as the "hidden" pigment in combination with a discharge pigment such as a black iron tannate, with or without a fat-soluble organic black dyestuff or a neutral black mixture of fat-soluble purple, green and yellow dyestuffs in such proportion that the combination of red "hidden" pigment and black "dominating" pigment, with or without black dye appears black. Properly formulated, this ink can be either applied to carbon paper or a typewriter ribbon which resemble ordinary black carbon paper or black ribbon and yield black copies or black typed texts. However, black typed texts or copies so made can be turned into red immediately upon contact with a strong oxidizing agent. For example, if it is desired to make certain words or numbers appear in red it merely is necessary to touch them with one of the commercial chemical ink eradicators, for example with an aqueous solution of sodium hypochlorite followed by diluted acid, or of potassium permanganate followed by oxalic acid, or of other oxidizing agents.

A typewriter ribbon, one half of its width inked along its entire length with an ordinary blue typewriter ink, and the other half of its width inked with a black-to-red color-convertible ink, as described above, will permit to type in three different colors: blue, black, and by contacting the black text with an oxidizing agent, red.

The same black-to-red color convertible ink, applied to one half of the ribbon, and an ink with a pigment combination consisting of an inert green lake toner with a violet discharge pigment such as phosphor tungstated methylviolet plus a little methylviolet base dissolved in the vehicle will produce a black-purple ribbon which will type either in black or in purple; the black being changeable into red and the purple being changeable into green upon contact with strong oxidizing agents; thus it becomes possible to type in four different colors, with one ribbon, in a regular typewriting machine.

The "dominant" pigments which I use are of the discharge type. They may be, for example, iron tannate, iron gallate, phosphor tungstated basic dyes such as Victoria blue base, methylviolet base, malachite green base and others, or natural organic pigments such as carmine lake, all of them reacting with oxidizing agents. I can also use dyestuffs which are precipitated on aluminum hydrates and are sensitive toward pH changes, such as methylviolet, turning light green and finally yellow in contact with diluted hydrochloric acid.

Dyestuffs of any chemical composition and structure can be used, subject to the requirements of solubility in the vehicle and susceptibility to the chemical agents employed to bring about the desired color conversion in the copy. The effects of these various agents on the dyestuffs is well known to the art and they require no experimentation for the purpose of my invention.

The "hidden" pigments used according to my invention may have any chemical composition, the only limiting attributes being insolubility in the vehicle and their resistance to the chemical agents employed. The pigments may be inorganic substances such as Milori blue (a special

kind of Prussian blue used in printing inks), vermillion, cadmium red, chrome green, chrome yellow, ferric oxides, tungsten colors, etc., or they may be color lakes or toners such as, e. g., lithol reds, Burma red, India red which are calcium and strontium salts respectively of rhodamine, etc.

The conventional vehicles for the coloring matters in transfer inks are mixtures of oils, fats, waxes, resins and other materials which are mostly water-insoluble and even water-repellent. Most of the chemical reactions useful to effect the color changes on which my invention is based proceed only in the aqueous solution or at least require the presence of water. For this reason and in order to apply my invention to best advantage, acting rapidly and yielding even results particularly if the copy is rather heavy, I employ vehicles which contain or which consist entirely of hydrophilic substances. The latter are not necessarily water-soluble but capable of absorbing and retaining a certain amount of water if in contact therewith and thus assure rapid, complete and uniform action by the chemical agents used to produce the color changes.

I prefer hydrophilic substances of rather low hygroscopicity. If the hygroscopicity of glycerin is compared with that of other substances by exposing them together under the same conditions to humid air, and weighing their increase of weight, and the hygroscopicity of glycerine is taken at 100. I prefer substances with a hygroscopicity of less than 30.

Another condition is that the hydrophilic substances which I use in the vehicle of said transfer inks are sufficiently compatible to be mixed with certain waxes, or fats, or oils in the desired ratios. Thus, I can use certain polyalkylene glycols of a molecular weight of about 500 and more. Certain polypropylene glycols of mol. weight 750 to 1300, for example, are liquid hydrophilic substances of low hygroscopicity which are compatible with carnauba wax, beeswax etc. Certain waxlike polyethylene glycols of molecular weight of more than 500 represent solid substances of that class that can be used for my purpose.

Numerous combinations of substances of fat, oil, wax and resin character can be used to produce the vehicle which must possess the physical properties suitable for application as a transfer and duplicating ink which must be serviceable by all standards demanded of the specific article (carbon paper, typewriter ribbon, inking pad, etc.) in its various uses. However, for the best embodiment of my invention it is advantageous that the vehicle have the additional quality, not required in the conventional transfer and duplicating inks of admitting aqueous reagents. If the vehicle itself is not sufficiently water-absorptive, adequate amounts of hydrophilic ingredients must be added to it.

Among other ingredients of hydrophilic character may be mentioned esters of polyhydric alcohols and ether-alcohols, such as the series of ether glycols known in the trade as di- to dodecaethylene glycols, with long-chain fatty acids such as lauric, stearic, myristic, oleic, linoleic or ricinoleic acid; ammonium, amine salts of the same acids; alkyl amines containing between 8 and 22 carbon atoms and their salts.

In some substances useful as vehicle ingredients, such as diethylene glycol mono stearate, diethylene glycol mono- or dioleate etc., the hydrophilic character can sufficiently be enhanced by the addition of small amounts of soaps.

EXAMPLE 1

Transfer ink for carbon paper

The following materials are intimately mixed, heated and thoroughly milled:

20 parts of triethanolamine stearate
22 parts of carnauba wax
20 parts of diethylene glycol oleate
36 parts of iron tannate (insoluble black discharge pigment)
2 parts of Burma red (insoluble red toner)

The black ink thus obtained is coated on a paper by one of the usual methods. Upon touching the black carbon copy with an aqueous solution of sodium hypochlorite, about 2% strength, followed by touching with dilute hydrochloric acid, and subsequent blotting, the color of the copy changes immediately from black to a permanent red.

EXAMPLE 2

Transfer ink for carbon paper

24 parts of morpholine stearate
25 parts of carnauba wax
17 parts of diethylene glycol oleate
20 parts of iron tannate
8 parts of India red (insoluble red toner)
2.7 parts of malachite green base
1.95 parts of Victoria blue base
.3 part of methylviolet base
1.05 parts of oil yellow (oil-soluble dyestuff)

are intimately mixed, heated and milled as in Example 1. The neutral black copy changes rapidly to red upon treatment with a 5% potassium permanganate solution followed by an aqueous 10% oxalic acid solution, or upon treatment with sodium hypochlorite solution as in Example 1.

EXAMPLE 3

Transfer ink for typewriter ribbon or inking pad

50 parts of diethylene glycol oleate or turkey red oil
35 parts of discharge black (iron tannate)
10 parts of Burma red (insoluble red toner)
5 parts of Oil Black GMBA 1831 (oil-soluble antrachinone dyestuff)

are intimately mixed and milled. A fabric of cotton, silk, nylon or other material in sheet or ribbon form, or a piece of felt is inked by one of the usual methods. The neutral black typed text or markings turn immediately into brilliant red upon contact with sodium hypochlorite solution, followed by diluted acid as specified in Example 1.

EXAMPLE 4

Transfer inks for four color typewriter ribbon

5 parts of ethylcellulose (alkyl contents 47%, viscosity 200 cps.)
50 parts of diethylene glycol oleate are heated and stirred together until the ethylcellulose is dissolved; then
5 parts of Oil Black GMBA 1831 (oil-soluble dyestuff) are added and dissolved;
10 parts of Burma red (red lake toner)
30 parts of iron tannate (discharge pigment) are added and all together thoroughly milled.

With this composition one half of the width of a ribbon is inked by one of the usual methods. The other half of the ribbon is inked with the

following ink composition, made in an analogous way:

45 parts of polypropylene glycol mol. w. 1250
10 parts of carnauba wax
5 parts of Victoria blue base
10 parts of green lake toner
30 parts of phosphor tungstated Victoria blue (discharge pigment)

One part of the ribbon types black which can be turned into red and the other part of the ribbon types blue that can be turned into green, both upon contact with sodium hypochlorite solution as used in Example 1.

EXAMPLE 5

Duplicating ink

15 parts of diethylene glycol stearate
10 parts of India red (red lake toner)
20 parts of methylviolet-aluminum hydroxide precipitate
47 parts of diethylene glycol oleate
8 parts of methylviolet base

are heated, intimately mixed and thoroughly milled. Purple copies made with this ink turn red upon contact with diluted hydrochloric acid of about ¼ N strength.

EXAMPLE 6

Inking pad ink

8 parts of purple lake toner (insoluble)
35 parts of carmine lake
5 parts of rhodamine base
52 parts of polypropylene glycol mol. w. 1250

The markings turn from red to purple upon contact with sodium hypochlorite solution as used in Example 1.

All quantities indicated in the above examples are in parts by weight.

It will be understood that, without departure

from the spirit of the invention or the scope of the claim, various modifications may be made in the specific expedients described. The latter are only illustrative and not offered in a restrictive sense, it being desired only such limitations shall be placed thereon as may be required by the state of the prior art.

I claim:

A transfer ink comprising a dispersed water-insoluble iron tannate pigment present in quantity sufficient to make the marking color of said ink substantially black, and at least one water-insoluble red pigment resistant to an aqueous oxidizing agent comprising ions selected from the group of hypochlorite and permanganate ions.

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