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⑤④ **Self-copying paper, particularly for composing printed forms arranged in stacked sheets and method of manufacturing it.**

⑤⑦ A self-copying paper for composing printed forms and other prints arranged in multiple stacked sheets comprises, on the back side thereof, a thermoplastic matrix in which is dissolved a leuco toner and, on the front side, a uniform layer including a toner developing agent. The toner on the back side of one sheet is adapted to be transferred by a localized pressure, to the front side of the next underlying sheet, and is developed there by the action of the developing agent.

**EP 0 017 823 A1**

This invention relates to a self-copying paper, particularly for composing printed forms and other prints arranged in multiple stacked sheets.

5 As is known, the term self-copying paper covers all those paper materials intended for the production of printed forms or other prints, as pre-arranged in the form of two or more stacked sheets which have been so treated as to result, under the application of localized pressure, in the impression of writings or any other graphic symbols being transferred in a condition of total readability to the front or upper side of all the sheets in the stack; self-copying paper differs from ordinary carbon paper in that a green sheet shows in practice no discoloration with respect to an untreated sheet.

15 Self-copying paper is constructed such as to present a covering layer on the back side thereof (commonly defined "CB" side) and a covering or coating on the upper or front side thereof (commonly defined "CF" side). In practice, a form comprising a stack of sheets in mutual overlapping relationship is so composed as to have the first or uppermost sheet with its front side untreated, thus constituting the "original", and the back side of the last or lowermost sheet untreated, the intermediate sheets having both their sides treated, respectively with a "CF" and "CB" coating.

25 According to the latest and most widely

accepted practice, the transfer effect is obtained through the utilisation of so-called microcapsules. These microcapsules contain a given amount of a coloring matter hereinafter called toner, which is in a clear or colorless (so-called "leuco") state, in order for the layer including such microcapsules to be correspondingly clear or colorless; the toner, however, is adapted to become activated or developed, thereby it acquires the desired color and imparts the desired visibility to the symbol or writing being transferred onto the paper, by a compound or substance which is present in the layer composition facing the one including the microcapsules, which upon manual or mechanical writing are in practice ruptured to allow the toner in leuco form out.

The use of microcapsules, while of widespread application in the production of self-copying paper, is not devoid of shortcomings, inasmuch as it requires special arrangements during the application of the layer containing the microcapsules and involves the use of a laminar air jet method to prevent incidental pressures, such as may occur during the application of the microcapsules onto the paper, from creating regions where an undesired color may appear already prior to the utilization of the printed forms themselves; on the other hand, that method permits no local area treatment.

Furthermore, the preparation of the layer containing the microcapsules is considerably expensive owing to the very presence of the micro-

capsules, and not always results in a product having a durable stability and an acceptable stability toward temperature variations.

Another drawback is that, in the majority of cases, it is necessary to utilize, for the paper material backing layer, papers which have already undergone surface treatments in order to prevent the migration of toner from one side of that sheet to the other; moreover, it generally happens that this type of paper has a relatively high thickness, which hinders the composition of forms with a high number of stacked sheets.

This invention sets out to eliminate the problems encountered in the past by providing a self-copying paper which allows ordinary paper, such as is normally available from the paper industry, to be used which, after the treatment, is still quite thin and, therefore, suitable for the production of a high number of transfer copies.

Within that general aim, it is a further object of the invention to provide a self-copying paper which can be manufactured by means of reduced size and cost apparatus, that is such as can be advantageously utilized by organizations and shops where form paper is printed prior and/or subsequently to the deposition of the layers on the sheet sides.

It is another object of this invention to provide a self-copying paper wherein the application

of the front and back layers is only allowed at predetermined areas of the sheet, to thus render self-copying just those portions which actually require to be so treated. The application operation, as mentioned, can be carried out at the printing shop which, by virtue of a continuous cycle operation, is advantageously enabled to produce forms printed in several colors and sensitized for self-copying at selected portions thereof.

10       A not unimportant object of this invention is to provide a self-copying paper which affords transfer copies capable of successfully withstanding ageing to sunlight and of resisting fading upon wetting.

15       These and other objects, such as will be apparent hereinafter, are achieved by a self-copying paper, particularly for composing printed forms and other prints arranged in multiple stacked sheets, according to the invention, characterized in that it comprises, on the back side thereof, a thermoplastic matrix in which there is dissolved or partly dissolved and partly dispersed a toner in the leuco form, and on the front side thereof, a uniform layer including a developer agent for developing said toner in the leuco form, said toner on the back side of one sheet being adapted to be transferred to the front side of the next underlying sheet by application of localized pressure and developed thereon by said developer agent contained on the front side of said next underlying sheet.

Further details will become more clearly

apparent from the following detailed description of some preferred embodiments of the self-copying paper according to the invention.

5       The back or "CB" layer which contains the  
toner in the leuco form comprises a thermoplastic  
matrix which is a microcrystalline wax matrix, a  
solvent of the toner which is compatible with said  
wax matrix, the whole having a melting point  
higher than 60°C and preferably in the 80 to 110°C  
10   range; understandably, the toner or mixture of  
toners in the leuco form will then be added,  
preferably dispersed through the mass.

      The high melting point is necessary in order  
to obtain a product which does not develop any  
15   unpleasant greasy feel when touched, even in the  
hottest climates and regions of the earth. Absolute  
compatibility, at least for the massive utilization  
ratios of wax matrix to solvent for the solid state  
toner, is a strict requirement in preventing  
20   solvent migration phenomena.

      The use of a microcrystalline wax matrix  
imparts to the layer an optimum feel quality and  
prevents a premature showing of the color as due  
to rubbing against the underlying sheet which is  
25   coated with a toner developer or activating agent  
constituting the layer "CF".

      The copy obtained with that back layer is  
resistant to water and photo-oxidation, since the  
reacted toner remains protected by the waxy  
30   product itself, which is insoluble in water and

forms a good sun radiation screen.

It will be apparent how such a wax matrix must be susceptible to micro-rupture under the mechanical action of a ballpoint pen or type-writing machine, which apply a localized pressure, such as to be transferred to the toner displaying layer or "CF" layer.

All these properties are achieved by employing as the waxy carrier high-melt microcrystalline paraffinic waxes or synthetic waxes of the Fischer-Tropsch type or solid chloro-paraffines which, owing to their chemical inertia (saponification number, 0), do not react with commercially available leuco toners, not even in their molten condition.

It is also contemplated that natural waxes may be used, such as montan and carnauba, or synthetic ones, such as S wax or OP wax, although the results to be obtained thereby, as relates to transparency and colorlessness of the layer, are inferior to those to be obtained through the use of synthetic waxes which only comprise carbon and hydrogen, or carbon, hydrogen and chlorine.

As toner solvents, chloro-paraffine, 1,2, diphenylethane, esters of phthalic acid, partly hydrogenated triphenyls, esters of salicylic acid, can be used either singly or in combination.

The leuco toners which can be utilized are those normally indicated in the pertinent literature, such as crystal violet lactone (a

compound of triarylmethane), blue of N-benzoyl-leucomethylene ( a compound of thiazine), and others, such as derivatives of xanthene (e.g., rodamine B-anilinelactame), spirodipyrane, and others.

The percentages by weight of the various components are normally within the following ranges of values:

|    |                      |        |
|----|----------------------|--------|
|    | microcrystalline wax | 50-80% |
| 10 | leuco toners         | 3-7 %  |
|    | toner solvents       | 10-30% |

Inert inorganic fillers may also be added, such as calcium carbonate or urea-formaldehyde resins, to vary the degree of whiteness and the opacity of the product.

A particularly preferred composition is the following:

Example 1

|    |                                      |       |
|----|--------------------------------------|-------|
|    | Fischer-Tropsch microcrystalline wax | 65    |
| 20 | (average molecular weight, 700)      |       |
|    | Crystal violet lactone               | 5     |
|    | Chloro-paraffine (amount in Cl 45%)  | 20    |
|    | Calcium carbonate                    | 10    |
|    |                                      | <hr/> |
|    |                                      | 100   |

Another formulation having a high rate of toner development is the following:

Example 2

|    |                                      |    |
|----|--------------------------------------|----|
|    | Fischer-Tropsch microcrystalline wax | 40 |
|    | (average molecular weight, 700)      |    |
| 30 | Crystal violet lactone               | 5  |



|                                  |       |
|----------------------------------|-------|
| 1,2-diphenylethane               | 15    |
| Urea-formaldehyde resin          | 5     |
| Microcrystalline paraffine,      | 35    |
| refined (melting point, 75-80°C) | <hr/> |
|                                  | 100   |

5

The products utilized to form the "CB" layer of Examples 1 and 2 should be applied to the paper at a temperature ranging from 100 to 120°C, in which range falls the most suitable viscosity value for the application.

10

On the front side of the sheet, there is provided a uniform layer, or "CF" layer, including a developing agent for the toner in the leuco form. The displaying layer or "CF" layer differs from those mentioned in the pertinent patent literature mainly because it employs, as the primary developing agent, micronized silicas of high purity (i.e. with a  $\text{SiO}_2$  content exceeding 95%, and preferably higher than 98% and above), obtained by pyrohydrolysis silicon tetrachloride. The extraordinary specific surface area of those silicas makes them compounds of exceptional reactivity, also but not exclusively, in combination with zinc chloride, which acts as a catalyst for the oxidoreduction reaction involved in the development of color.

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Since the use of high purity silicas, notwithstanding their ability to develop the color instantaneously, is not sufficient to ensure durability of the color brilliance, it becomes necessary to employ, as secondary developers,

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phenolic products such as phenol-formaldehyde resins (in particular the ones prepared by polycondensation of p-phenyl phenol and formaldehyde), diphenylolpropane, and esters of 3,4,5-trioxybenzoic acid.

For the application of such products, a liquid phase must be made available wherein the developing agents are dissolved and/or dispersed.

That liquid phase comprises essentially ketones, alcohols, alcoholethers, particularly effective being the acetone/methanol pair which, having a high evaporation rate, allows the product to be applied by means of a machinery of comparatively small size and low cost, including a drying system with a length of 2 to 3 meters, adequate to evaporate the solvent while having an output rate which reach 200 to 250 m/minute.

In order for the product spread onto the paper to be perfectly anchored thereto and to show no indications of inconsistency to the touch, it is necessary to introduce in the formulations suitable amounts of synthetic resins effective to improve the adhesion of the layer to the front side, among such resins the use of cellulosic ethers being particularly advantageous.

The presence of silica, colloiddally dispersed in the solvents, and the use of binders which are completely dissolved in the solvents, may raise the flash point of the product to values exceeding 21°C, even when solvents are employed having per se a neatly lower flash point, such as methanol

and acetone.

The percentages of the dissolved and/or dispersed solids ranges from 20 to 40% by weight of the product. The zinc chloride to silica ratio  
5 is in the 0.00 to 0.4% range.

A further important feature is the use of high-boiling solvents for the leuco toners which are retained by the silica owing to the strong oil absorbency that characterizes it. Such solvents,  
10 e.g. chloroparaffines, partly hydrogenated tri-phenyl, esters of phtalic acid, favor and accelerate the color development process because, being preferably adsorbed by the silica, they favor its contact with the toner upon application of a  
15 localized mechanical action or pressure which causes the "CB" product to separate locally and contact the "CF" layer: it is known, indeed, that the color developing reaction occurs preferably in the liquid phase, that is with the toner  
20 dissolved.

This explains the high effectiveness of the silica/leuco toner solvent combination.

Two preferred compositions for the "CF" layer are now given here below.

25 Example 3

|                                 |    |
|---------------------------------|----|
| Acetone                         | 20 |
| Methanol                        | 50 |
| Diphenylolpropane               | 5  |
| p-phenylphenol and formaldehyde |    |
| 30 polycondensation product     | 5  |

|    |   |       |
|----|---|-------|
|    | Chloroparaffine (Cl rate 45%)                         | 2     |
|    | No. 7 Ethylcellulose                                  | 7     |
|    | Silica from hydrocracking ( $\text{SiO}_2 > 98.5\%$ ) | 7     |
|    | $\text{ZnCl}_2$                                       | 2     |
| 5  | Kaolin  | 2     |
|    |   | <hr/> |
|    |   | 100   |
|    | <u>Example 4</u>                                      |       |
|    | Methylisobutylketone                                  | 14    |
|    | Isopropanol   | 60    |
| 10 | $\text{ZnCl}_2$                                       | 3     |
|    | Silica from hydrolysis ( $\text{SiO}_2 > 98.5\%$ )    | 7     |
|    | No. 7 Ethylcellulose                                  | 6     |
|    | Diphenylolpropane                                     | 5     |
|    | Propylgallate   | 2     |
| 15 | Partly hydrogenated triphenyl                         | 3     |
|    |   | <hr/> |
|    |   | 100   |

The developer layers with the features provided by this invention are particularly suitable for developing color from donor "CB" layers, also provided by the invention, but not only so, because they may be advantageously employed also with conventional "CB" layers including microcapsules.

The forms or prints to be obtained with the self-copying paper according to the invention have, as usual, the front side of the first or uppermost sheet untreated, and the back side of the last or lowermost sheet also untreated, whereas both sides of the intermediate sheets are treated, thereby upon application of a localized pressure as due

to manual or mechanical writing, the back layer is transferred to the underlying front layer, thus producing a development of the toner in the leuco form, which in a very short time becomes visible.

5           Therefore, it will be appreciated from the foregoing that the invention achieves its objects and in particular it should be noted that, by eliminating the microcapsules and replacing them in practice with a layer of a crystalline wax  
10 material, in addition to affording a drastic reduction of the production costs, the invention ensures a product of improved quality, both as regards the sharpness of the resulting copies, and stability in time.

15           The invention as described is susceptible to numerous modifications and variations, all of which fall within the purview of the instant inventive concept.

20           Moreover, all of the details may be replaced with other technically equivalent elements.

C L A I M S

1           1. A self-copying paper particularly for composing  
2     printed forms and other prints arranged in multiple  
3     stacked sheets, characterized in that it comprises, on  
4     the back side thereof, a thermoplastic matrix in which  
5     there is dissolved or partly dissolved and partly  
6     dispersed a toner in the leuco form, and on the front  
7     side thereof, a uniform layer including a developer  
8     agent for developing said toner in the leuco form, said  
9     toner on the back side of one sheet being adapted to be  
10    transferred to the front side of the next underlying  
11    sheet by application of localized pressure and developed  
12    thereon by said developer agent contained on the front  
13    side of said next underlying sheet.

1           2. A self-copying paper according to Claim 1, char-  
2     acterized in that the layer provided on said back side  
3     comprises at least one organic solvent for the leuco  
4     toners adapted to be mixed in the liquid state with  
5     the material of said thermoplastic matrix.

1           3. A self-copying paper according to the preceding  
2     claims, characterized in that said thermoplastic matrix  
3     incorporating said organic solvent in which said toner  
4     in the leuco form is dissolved is adapted to solidify  
5     in a substantially microcrystalline form.

1           4. A self-copying paper according to one or more of  
2     the preceding claims, characterized in that said thermo-  
3     plastic matrix comprises substantially microcrystalline  
4     wax substantially consisting of carbon and hydrogen,  
5     or carbon, hydrogen and chlorine.

1           5. A self-copying paper according to one or  
2 more of the preceding claims, characterized in that  
3 said layer provided on said front side comprises  
4 high purity micronized silicas.

1           6. A self-copying paper according to one or  
2 more of the preceding claims, characterized in that  
3 it comprises, in combination with said micronized  
4 silica, zinc chloride.

1           7. A self-copying paper according to one or  
2 more of the preceding claims, characterized in that  
3 it comprises, in combination with said high purity  
4 micronized silica, solvents for the leuco  
5 toners.

1           8. A self-copying paper according to one or  
2 more of the preceding claims, characterized in that  
3 it comprises, in combination with said high purity  
4 micronized silica, phenolic products effective to  
5 ensure the persistence in time of the symbols  
6 written.

1           9. A self-copying paper according to one or  
2 more of the preceding claims, characterized in  
3 that the product applied to said front side of said  
4 sheets has a flash point exceeding 21°C, even if  
5 solvents are used of a lower flash point.

1           10. A method of manufacturing a self-copying  
2 paper as claimed in the preceding claims,  
3 characterized in that said thermoplastic matrix  
4 incorporating said toner in the leuco form is  
5 applied to the sheet in a molten state.

1           11. A method according to Claim 10, character-

2    ized in that said uniform layer provided on said  
3    front side is subjected, following the application  
4    thereof, to a drying treatment in  
5    which . the treated sheet undergoes continuous heat-  
6    ing within temperature and time limits in ranges  
7    required to eliminate said organic solvent.



| DOCUMENTS CONSIDERED TO BE RELEVANT                        |  |  | CLASSIFICATION OF THE APPLICATION (Int. Cl. <sup>3</sup> )   |
|--|--|--|--|
| Category   | Citation of document with indication, where appropriate, of relevant passages  | Relevant to claim                                  |  |
| X  | <u>FR - A - 2 302 200</u> (KORES)<br><br>* Page 1, lines 1-6; page 3,<br>lines 17-39; example 1; claims *<br>---                       | 1,6  | B 41 M 5/12<br>B 41 M 5/22   |
| X  | <u>US - A - 2 646 367</u> (DAVIS et al.)<br><br>* Column 4, line 13 to column 5,<br>line 47; column 6, lines 47-64;<br>claims *<br>--- | 1-4, 11,<br>12                                     |  |
|  | <u>GB - A - 1 147 480</u> (N.C.R.)<br><br>* Column 2, lines 38-61 *<br>---   | 5  | TECHNICAL FIELDS<br>SEARCHED (Int.Cl. <sup>7</sup> )   |
|  | <u>US - A - 3 684 549</u> (SHANK)<br><br>* Column 3, lines 12-72;<br>column 5, lines 21-29; examples *<br>---                          | 1-4, 11,<br>12                                     | B 41 M 5/12<br>B 41 M 5/22   |
|  | <u>BE - A - 756 601</u> (WIGGINS TEAPE)<br><br>* Page 4, lines 3-28; example 3 *<br>---  | 6,7,9  |  |
|  | <u>US - A - 3 672 935</u> (MILLER et al.)<br><br>* Claims *<br>---   | 8  |  |
| A  | <u>FR - A - 2 305 206</u> (MEAD)<br><br>* Page 10, line 27 to page 14,<br>line 23 *<br><br>-----                                       | 1  | CATEGORY OF<br>CITED DOCUMENTS<br><br>X: particularly relevant<br>A: technological background<br>O: non-written disclosure<br>P: intermediate document<br>T: theory or principle underlying<br>the invention<br>E: conflicting application<br>D: document cited in the<br>application<br>L: citation for other reasons |
| The present search report has been drawn up for all claims |  |  | &: member of the same patent<br>family,<br>corresponding document  |
| Place of search<br><br>The Hague                           |  | Date of completion of the search<br><br>08.07.1980 | Examiner<br><br>AMAND  |