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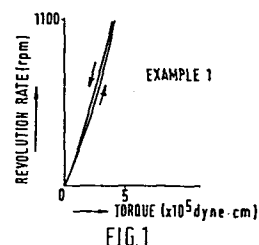
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54 Colour-developer sheet for carbonless copying system.

57 A colour-developer sheet, for use in a carbonless copying system, having a coating comprising a solid particulate activated clay with, preferably, a dispersant therefor; calcium carbonate; and a binder of polyvinyl alcohol and styrene-butadiene.



COLOUR-DEVELOPER SHEET FOR CARBONLESS COPYING SYSTEM.

This invention relates to colour-developer sheets for use in a carbonless copying system, and more particularly, to an improved colour-developer sheet characterised by using in the ^{preparation thereof} ~~the~~ a coating liquid consisting essentially of solid particulate activated clay which has been previously mixed together with a dispersing agent, calcium carbonate added for replacement of part of the activated clay, and a binding agent of polyvinyl alcohol and a styrene-butadiene latex.

Carbonless copying sheets of paper are well known as disclosed for example in U. S. Patents No. 2,712,507, No. 2,730,465 and No. 2,730,457. Such known copying paper sheets result from the use of microcapsules containing solutions in which colourless organic compounds having electron-donative, non-adsorptive and colour-forming reactive properties (hereinafter referred to as "colour-formers") are dissolved in organic solvents, and adsorptive substances having electron-acceptive and co-reactive properties (hereinafter referred to as "colour-developers").

Microencapsulation is effected by known processes such as ~~con~~cervation, in situ polymerisation, interfacial polymerisation or the like.

Eligible examples of the colour-developers in the prior art practice include malachite green lactone, crystal violet lactone, benzoyl leuco methylene blue, rhodamine B lactam, 3-dialkylamino-7-dialkylamylfluoran, 3-methyl-2,2-spiropibenzo[f]chromene and the like.

Exemplary of the colour-developers in the prior art practice are an inorganic group including solid acids such as acid clay, activated clay, attapulgite, zeolite, bentonite and the like; and an organic group including phenolic resins such as p-tert-butylphenol resin, p-phenylphenol resin, p-octylphenol resin and the like; organic compounds such as succinic acid, tannic acid, malonic acid, gallic acid and the like, or metal salts thereof; and aromatic carboxylic acids such as benzoic acid, salicylic acid, substituted salicylic acids, naphthoic acid, diphenic acid and the like, or metal salts thereof.

Of the colour-developers exemplified above, activated clay, phenolic resins and substituted salicylic acid have been in actual use in respect of their respective dominant characteristics.

It has now been found that phenolic resins and substituted salicylic acid (salts) of an organic class may operate to allow coating liquids to be applied at a higher concentration, but do not give rise to good printability. Furthermore, these two colour-developers are costly because they are derived from chemical syntheses. Activated clay of an inorganic class is found to work out in improving printability such for example as ink adsorption and to be economically inexpensive. However, one disadvantage experienced with such activated clay colour-developer is that a coating liquid prepared therefrom is liable to become gelled, with ultimate difficulty in sheet coating at a higher concentration.

As is taught in Japanese Patent Publications No. 41-2373, No. 41-7622 and No. 42-8811, activated clay useful as a colour-developer is one having a surface area of more than $200 \text{ m}^2/\text{g}$ and obtained by treatment of acid clay or any other similar type of clay with mineral acid to elute any acid-soluble basic components such as alumina, iron and the like. The activated clay colour-developer thus produced, even if mixed with salts such for example as zinc, magnesium and the like, may be used successfully.

As is readily clear from x-ray examination, activated clay is of an amorphous shape and has a large specific surface area. Accordingly, activated clay is substantially characteristically different from pigments commonly used for coating sheets of paper. When activated clay is actually dispersed in water, a greater amount of water is required to complete the dispersion due to the shape, surface activity and other factors inherent to the powder particles of the activated clay.

Although kaolin clay typical of sheet coating, when dispersed in water, can retain its fluidity up to a concentration of more than 70%, activated clay becomes highly viscous at a concentration in the vicinity of 45% and encounters reduced fluidity, resulting in gelled condition. Now, it is desired that sheet coating be performed at a higher concentration for purposes of increased rates of production and savings of energy. For the foregoing reasons, however, a highly concentrated coating liquid is difficult to attain with

activated clay, and an air knife coating system is currently employed using a coating liquid of low concentration.

An object of the present invention is to provide means to reduce the viscosity of a coating liquid to be applied to a colour-developer sheet for use in a carbonless copying system and to otherwise improve the fluidity of the coating liquid so as to be rendered adequate for application at a higher concentration.

An aspect of this invention resides in applying a coating liquid onto a colour-developer sheet, which liquid consists essentially of solid particulate activated clay, admixed previously with a dispersant, calcium carbonate, and a binder of polyvinyl alcohol and a styrene-butadiene latex.

The practice of the present invention provides a substantial improvement wherein considerably superior dispersion and fluidity of activated clay in water as well as viscosity reduction of the resulting coating liquid are achieved, with the result that higher concentration sheet coating is made applicable. Such improvement leads not only to simplified adjustment of the quantities of the coating liquid to be applied, and hence improved coating operation, but also to increased energy-saving and productivity. Another performance advantage is that a sheet of paper thus coated is of good quality with excellent smoothness and resistance to smudge (blurry spots arising from rubbing its coated sheet surface) and with improved surface strength.

In general, activated clay useful for the practice of the invention is produced by treating acidic clay with a suitable acid, followed by washing with water, drying and then grinding of the acid treated clay.

There are various methods of mixing a dispersant useful in the invention together with the activated clay. A first method is to treat acidic clay with an acid and to add an aqueous solution of the dispersant to the resulting clay after being washed with water. A second method is to mix particulates of the dispersant with the acid treated clay prior to drying, and a third method lies in admixing the particulate dispersant with the acid treated clay after drying, followed by subsequent grinding of the admixture. Alternatively, the sequence of a fourth method is such that the dispersant particulates are admixed with the acid treated clay before grinding. While any of the methods of the type described may be used satisfactorily, no limitation should not be considered to be imposed upon these methods.

Eligible dispersants according to the invention are e.g. sodium tripolyphosphate, sodium hexametaphosphate, sodium pyrophosphate, sodium silicate and the like, all of which are of an inorganic class; and carboxylates (acrylic acid salt, etc.), maleates (styrene-maleic anhydride salt, etc.), sulfonates (naphthalene-sulfonic acid salt, etc.) and the like, all of which are of an organic class.

Suitable amounts of the dispersant for the practice

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of the invention fall e.g. in the range of 0.1 to 15%, preferably 1.0 to 8.0%, based on the weight of activated clay. Smaller amounts may not give satisfactory results, whereas greater amounts may result in reduced colour-forming concentration.

Among the above specified dispersants, sodium pyrophosphate, sodium tripolyphosphate and sodium hexametaphosphate are preferred which exhibit significantly superior activity.

Calcium carbonate according to the invention may ^{e.g.} be used both in heavy form and in light form. Particularly preferable are light calcium carbonate which is cubic in shape and has a particle diameter of 0.1 to 1.0 μ , and heavy calcium carbonate which has an average particle diameter of 1.0 μ , but these two specific forms are not limiting to the invention.

Suitable amounts of calcium carbonate are ^{e.g.} in the weight range of 5 to 25%, preferably 10 to 15%, based on the total of carbonate and clay, whose amounts are ^{thus} ~~are~~ from 95 to 75%, and 90 to 85%, respectively. Less amounts of calcium carbonate may exert no desirable effect, while greater amounts may reduce colour-forming concentration and thereby result in unsatisfactory coating liquid for application onto a colour-developing sheet.

Polyvinyl alcohol according to the invention preferably has a saponification value of more than 98% by mole and a polymerisation degree of less than 700. Other values

may give poor fluidity of a coating liquid. Suitable amounts of polyvinyl alcohol are e.g. 1.0 to 10.0%, preferably 2.5 to 6.0%, based on the weight of activated clay. Smaller amounts may achieve no sufficient fluidity, and greater amounts may result in extremely viscous coating liquid.

Styrene-butadiene latexes according to the invention preferably contain the essential ingredient styrene in an amount of 55 to 65% by weight of the polymer. Departure from this range may involve reduced water resistance of a coated paper sheet and adversely affect printability of the sheet.

Within the scope of this invention, carboxyl-modified styrene-butadiene latexes resulting from copolymerisation of unsaturated carboxylic acids such as acrylic acid, methacrylic acid, itaconic acid and the like may also be used with satisfactory results. Suitable amounts of the styrene-butadiene latex give e.g. 5.0 to 20.0% ^{polymer} based on the weight of activated clay. An amount of 8.0 to 15.0% by weight is most satisfactory. Less amounts may not work well in improving fluidity of a coating liquid. Greater amounts may reduce colour-forming concentration.

With a coating liquid contemplated by the invention for use on a colour-developer sheet, which coating liquid

consists essentially of activated clay, calcium carbonate, polyvinyl alcohol, and a styrene-butadiene latex, it is apparent that dispersion and fluidity of the coating liquid at a higher concentration are greatly enhanced, thus facilitating improved coating operation. This is attributable from the fact that the quantities of the coating liquid to be applied can be controlled in a simple way, and that it is easily possible for the coating liquid to be supplied to and recovered from a coater head. An additional advantage is that a substrate such as paper coated with the coating liquid is at optimum almost completely smudge-proof since such coated substrate is of good smoothness with minimal capsular rupture even when brought into rubbed contact with its corresponding capsulated surface. The substrate shows a further improvement in its surface strength.

The invention will be further described by way of the following examples, in which was used commercially available carbonless copying top paper "Mitsubishi NCR Paper Top-40" as the colour-former sheet.

Preparation of Carbonless Copying Colour-developer Sheet

Inventive Example 1

12.5 parts by weight of heavy calcium carbonate (made by Bihoku Funka K. K., Softon No. 2200) was dispersed in 60 parts by weight of water, followed by addition of 50 parts by weight of an aqueous solution of 10% polyvinyl alcohol (made by Kuraray K. K., saponification value: 98.5% by mole, polymerisation degree: 500). To this admixture was slowly added with stirring 87.5 parts by weight of activated clay which had been in advance prepared by homogenising 3 parts by weight of particulate sodium pyrophosphate to 100 parts by weight of particulate activated clay. 10 parts (solid) by weight of a styrene-butadiene latex (made by Dow Chemical Co., Dow 670, styrene: about 70% by weight) was then added, and stirring was continued. 20% sodium hydroxide was added to adjust the admixture to a pH of 9.5.

The resulting liquid was applied by a blade coater to paper of 40 g/m² in a coat weight of 8 g/m² (solid).

Comparative Example 1

1.0 parts by weight of sodium pyrophosphate was completely dissolved in 60 parts by weight of water, followed by addition of 50 parts by weight of an aqueous solution of 10% polyvinyl alcohol (PVA-105). To this admixture was slowly added with stirring 100 parts by weight of activated clay. 10 parts (solid) by weight of an acrylic latex (made by Toyo Ink K. K., Tokryl S-20, copolymer of an acrylic ester and styrene) was then added, and stirring was continued. 20% sodium hydroxide

was added to adjust the admixture to a pH of 9.5.

The resulting liquid was applied by a blade coater to paper of 40 g/m² in a coat weight of 8 g/m².

Comparative Example 2

1.0 part by weight of sodium pyrophosphate was completely dissolved in 60 parts by weight of water, followed by addition of 50 parts by weight of an aqueous solution of 10% oxidised starch (made by Nippon Shokuhin K.K., MS-3800). To this admixture was slowly added with stirring 100 parts by weight of activated clay. 10 parts (solid) by weight of a styrene-butadiene latex (Dow 670) was then added, and stirring was continued. 20% sodium hydroxide was added to adjust the admixture to a pH of 9.5.

The resultant liquid was applied by a blade coater to paper of 40 g/m² in a coat weight of 8 g/m².

Test Results

The properties of the coating liquids and colour-forming paper sheets were tested and determined as follows:

1. Coating Liquids

o Viscosity

Measurement was made using a B-type viscometer (made by Tokyo Keiki K. K.), under the conditions: rotor, No. 4; rpm, 60, time, 1 minute (cps: centipoise). In Figs. 1 to 3 there are

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shown the viscosity curves of the coating liquids obtained in Inventive Example 1 and Comparative Examples 1 and 2 and measured using a Hercules II-type High-shear viscometer (made by Nippon Rigaku Kogyo K. K.).

o Solid Content

Measurement was made under the conditions: temperature, 110°C; and drying time, 16 hours.

2. Colour-developer Sheets

o Smoothness

Measurement was made using a Beck smoothness tester (made by Kumagaya Riki K.K.). This property improves as the numerical values become larger.

o Smudge Resistance

Determination was made by measuring the reflectance of the tested colour-developer sheets after being brought into rubbed contact with the above noted colour-former sheets at a load of 300 g/m². The measurement was performed using a colour difference meter (made by Nippon Denshoku). This property becomes greater as the numerical values increase.

o Surface Strength

Measurement was made using an IGT tester (made by Kumagaya Riki K. K.) under the conditions: ink, IPI No. 4; and spring, B. This property was designated by the marks ○ and △.

○ Colour-forming Concentration

Determination was made by measuring the following values of the tested colour-developer sheets after being brought into face to face contact with the above stated colour-former sheets and calendered at a pressure of 96 kg/cm.

$$\text{Colour concentration (\%)} = \frac{\text{Reflectance of coloured area}}{\text{Reflectance of uncoloured area}} \times 100$$

(one hour after calendering)

Table 1 (Coating Liquids)

	Viscosity (cps)	Solid Content (%)	Fluidity
Inventive Example 1	510	45.2	Good
Comparative Example 1	5,600	45.0	Gelled
Comparative Example 2	7,800	45.2	Gelled

It is evident from Table 1 that despite being substantially equal in solid content, the coating liquid of Inventive Example 1 is of considerably low viscosity and also is of good fluidity as compared to the coating liquids of Comparative Examples 1 and 2. As shown in Figs. 1 to 3 the comparative liquids are more viscous than the inventive liquid at high-speed revolution rate and become gelled at low-speed revolution rate.

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Table 2 (Colour-developer Sheets)

	Smoothness (sec)	Smudge Resistance	Surface Strength	Colour- forming Concentration
Inventive Example 1	91	91.2	○	27.2
Comparative Example 1	40	83.5	⊗	27.5
Comparative Example 2	38	82.7	⊗	28.0

As can be understood from Table 1 and 2 and Figs. 1 to 3, the use of activated clay admixed previously with a dispersant, calcium carbonate, polyvinyl alcohol and a styrene-butadiene latex is effective in imparting not only satisfactory viscosity to a coating liquid but also increased smoothness, smudge resistance and surface strength to a colour-developer sheet.

4. BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1 to 3 are rheograms of a coating liquid embodying the present invention and illustrated in Inventive Example 1 and coating liquids exemplified in Comparative Examples 1 and 2.

C L A I M S

1. A colour developer sheet, for use in a carbonless copying system, in the preparation of which there is used a coating liquid comprising i) a solid particulate activated clay preferably pre-mixed with a dispersant, ii) calcium carbonate and iii) a binder of polyvinyl alcohol and a styrene-butadiene latex.

2. A colour-developer sheet or set for use in a carbonless copying system which comprises, in combination, microcapsules containing an electron-donative, colourless organic compound, and an adsorptive substance comprising activated clay capable of developing colour upon adsorption of said colourless organic compound, in the preparation of which there is used a coating liquid consisting essentially of solid particulate activated clay, inter-mixed previously with a dispersant, in the range of 95 to 75% by weight, calcium carbonate in the range of 5 to 25% by weight, and a binder of polyvinyl alcohol and a styrene-butadiene latex, percentages being related to the total of clay and carbonate.

3. A colour-forming sheet or set according to claim 1 or 2, wherein said polyvinyl alcohol has a saponification value of not less than 98% by mole and a polymerisation degree of not more than 700.

4. A colour-developer sheet or set according to claim 1, 2 or 3, wherein said polyvinyl alcohol is present in an amount of 1 to 10 % based on the weight of said activated clay, and said styrene-butadiene latex is present in an amount giving 5 to 20 % polymer based on the weight of said activated clay.

5. A colour-developer sheet or set according to any preceding claim, wherein said coating liquid has a concentration of not less than 45% by weight activated clay.

6. A colour-developer sheet or set according to claim 2 or claim 3, 4 or 5 as appendent to it, wherein the relative amounts of clay and carbonate are 90 to 85% and 10 to 15%.

7. A colour-developer sheet or set according to claim 4 or claim 5 as appendent to it, wherein the amount of polyvinyl alcohol is 2.5 to 6% and the amount of styrene-butadiene polymer is 8 to 15%.

8. A colour-developer sheet or set according to any preceding claim, wherein the styrene-butadiene polymer contains 55 to 65% by weight styrene.

9. A colour-developer sheet or set according to any preceding claim, wherein the styrene-butadiene is a modified polymer resulting from co-polymerisation with

acrylic acid, methacrylic acid, itaconic acid or other copolymerisable unsaturated carboxylic acid.

10. A colour-developer sheet or set according to any preceding claim, wherein the carbonate is light calcium carbonate cubic in shape and of particle size in the approximate range 0.1 to 1 micron or heavy calcium carbonate of average particle size approximately 1 micron.

11. A colour-developer sheet, for use in a carbonless copying system, having a coating comprising a solid particulate activated clay with, preferably, a dispersant therefor; calcium carbonate; and a binder of polyvinyl alcohol and styrene-butadiene.

12. A colour-developer sheet according to claim 11, wherein the relative amounts and/or characteristics of said clay, carbonate, polyvinyl alcohol and styrene-butadiene are as given in any one of claims 2 to 4 and 6 to 10.

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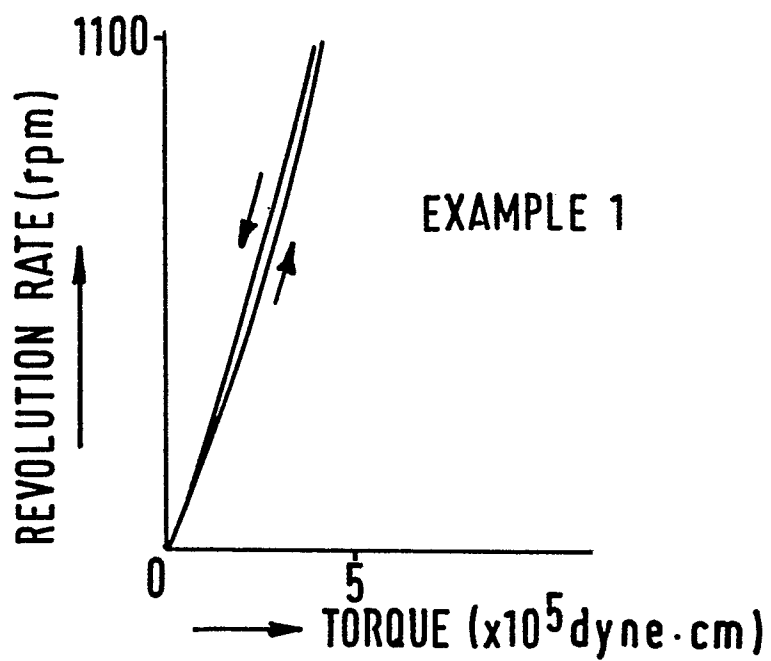


FIG. 1

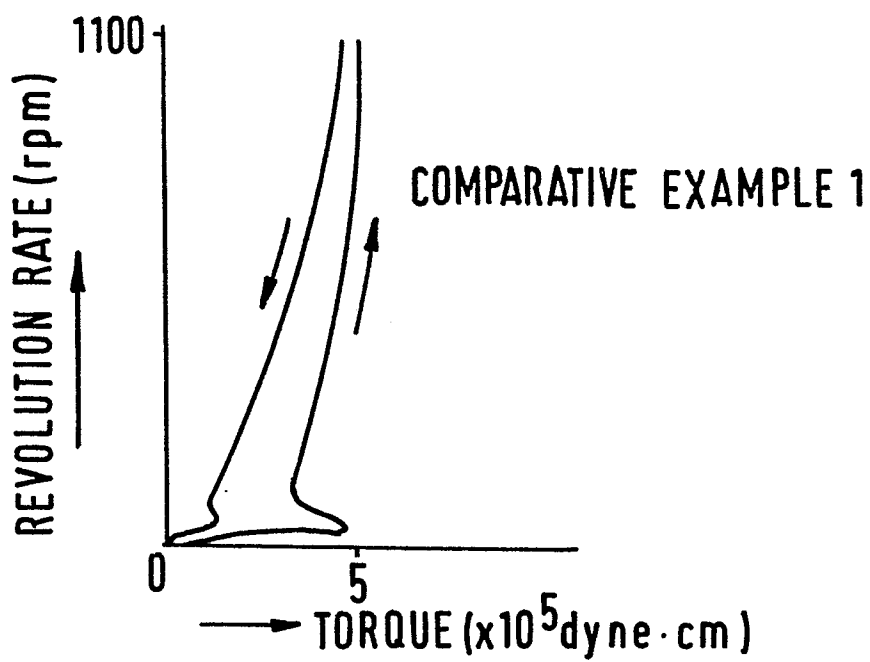


FIG. 2

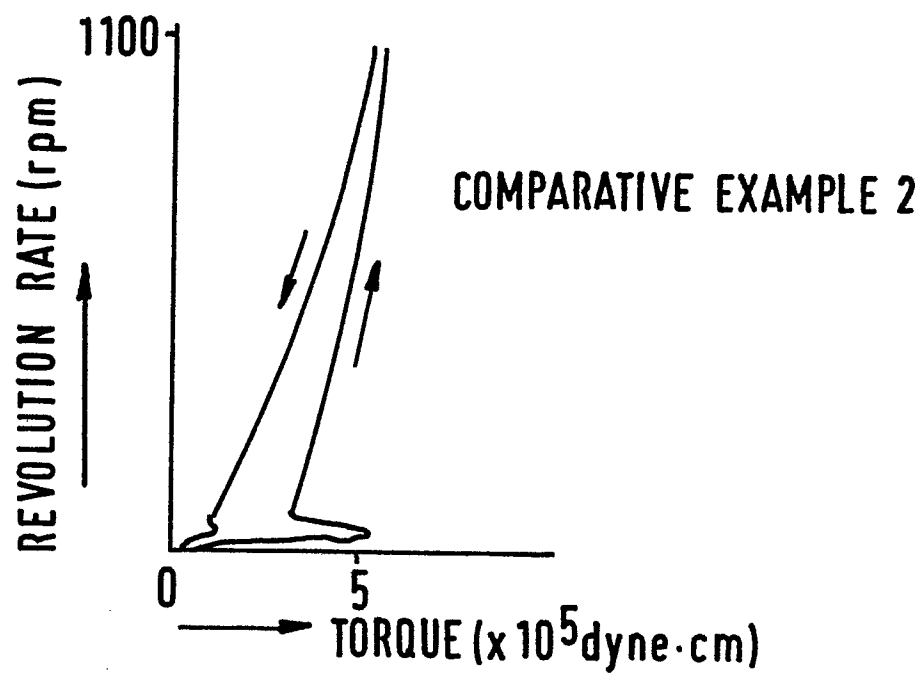


FIG. 3



DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	<u>GB - A - 2 050 407</u> (MITSUBISHI PAPER MILLS) * Claims; page 1, lines 84-89 * --	1-12	B 41 M 5/12
X	<u>GB - A - 2 028 888</u> (MITSUBISHI PAPER MILLS) * Page 1, lines 30-35; claims; examples * --	1-12	
X	<u>US - A - 3 223 546</u> (G.H. HEMSTOCK) * Column 6, line 65 - column 7, line 16 * --	1-12	TECHNICAL FIELDS SEARCHED (Int.Cl. 3) B 41 M 5/00
X	<u>DE - B - 1 152 429</u> (NCR) * Column 3, lines 32-43; claims * --	1-12	
X	<u>US - A - 3 622 364</u> (MIZUSAWA KAGAKU KOGYO) * Column 2, lines 37-67 * --	1-12	
A	<u>DE - C - 1 001 292</u> (NCR) * Column 2, line 46 - column 3, line 49 * & GB - A - 760 080 ----	1	CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document
X	The present search report has been drawn up for all claims		
Place of search The Hague		Date of completion of the search 26-04-1982	Examiner RASSCHAERT