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Carbonless paper for ink jet printing.

The invention relates to a carbonless paper and to an ink jet printing process employing the carbonless paper. The ink jet printing process involves a process for generating images which comprises incorporating into an ink jet printing apparatus a carbonless paper set which comprises a first sheet comprising a support containing a color developer capable of reacting with a color former to produce a color image, and a second sheet comprising a support coated with the color former; characterised in that said color developer comprises high surface area silica particles, and forming an image on the first sheet by causing ink to be expelled in droplets on a surface containing the color developer; and forming an image on the second sheet by causing ink to be expelled in droplets onto the surface opposite to that coated with the color former.

In a preferred embodiment there is provided a carbonless paper set which comprises a first sheet comprising a support containing a color developer capable of reacting with a color former to produce a color image, and a second sheet comprising a support coated with the color former, characterised in that said color developer comprises silica particles having a surface area of from about 100 to about 195 square meters per gram.

The present invention is directed to ink jet printing processes and, more particularly, to ink jet printing processes employing recording sheets coated with a layer of color developer that is suitable as a component of a carbonless paper set.

Carbonless paper sets generally are stacks of at least two sheets of paper wherein the application of pressure in imagewise fashion on the top sheet, typically by handwriting or typing, results in formation of a corresponding image on the underlying sheets, so that copies are formed as the image is generated on the top sheet. Carbonless paper sets typically comprise a top sheet of paper, on the bottom surface of which is coated a first composition, and a bottom sheet, on the top surface of which is coated a second composition. The first and second compositions are in contact with each other when the top and bottom sheets are placed in stack formation, and generally are of a nature such that application of pressure to the top sheet of the stack at a specified location causes interaction between the first and second compositions that results in the formation of a colored area on the bottom sheet at the location at which pressure was applied. Intermediate sheets can be located between the top and bottom sheets, wherein each intermediate sheet is coated on its top surface with the second composition and on its bottom surface with the first composition; application of pressure to the top sheet then results in the formation of a colored area at the location at which pressure was applied on each of the intermediate sheets and on the bottom sheet.

An example of a carbonless paper set is disclosed in U.S. Patent 3,843,383 (Ishige et al.), the disclosure of which is totally incorporated herein by reference. This patent discloses a recording sheet comprising a support having thereon a layer of color developer capable of reacting with a substantially colorless color former to form colored images. The paper set generally comprises a top sheet coated with microcapsules containing a color former solution, a bottom sheet coated with a color developer solution in a binder, and, in some instances, middle sheets coated on one side with the color developer and on the other side with the color former microcapsules. Alternatively, the color former microcapsules and the color developer can be applied to the same surface of a paper. The color developer comprises a clay into which is incorporated at least one aromatic carboxylic acid or alkali metal salt thereof, and, optionally, acidic resins or inorganic pigments such as metal oxides, metal hydroxides, or metal carbonates. Suitable clays include acidic clay, active clay, attapulgite, zeolite, bentonite, kaolin, silicic acid, synthetic silicic acid, aluminum silicate, zinc silicate, colloidal silicic acid, and the like. The clay and the aromatic carboxylic acid or alkali metal salt thereof are formed into a coating solution which is then applied to paper. The color former is dissolved in a solvent and encapsulated in

microcapsules, or is dissolved in a solvent and mixed with a binder. Contacting a sheet coated with microcapsules containing the color former under pressure with a sheet coated with the color developer results in formation of a color image. Other patents disclosing carbonless paper of this type include U.S. Patent 2,712,507 and U.S. Patent 2,730,456, the disclosures of which are totally incorporated herein by reference. Alternatively, as disclosed in U.S. Patent 2,730,457, the disclosure of which is totally incorporated herein by reference, the color former microcapsules and the color developer of a carbonless paper can be applied to the same surface of a paper sheet. Other configurations of color former, color developer, and a pressure-releasable liquid solvent are possible, including, for example, those disclosed in U.S. Patent 3,672,935, the disclosure of which is totally incorporated herein by reference. Additional patents disclosing carbonless papers and materials suitable for carbonless paper applications include U.S. Patent 2,417,897, U.S. Patent 3,672,935, U.S. Patent 3,681,390, U.S. Patent 4,202,820, U.S. Patent 4,675,706, U.S. Patent 3,481,759, U.S. Patent 4,334,015, U.S. Patent 4,372,582, U.S. Patent 4,334,015, U.S. Patent 2,800,457, U.S. Patent 2,800,458, U.S. Patent 3,418,250, U.S. Patent 3,516,941, U.S. Patent 4,630,079, U.S. Patent 3,244,550, U.S. Patent 3,672,935, U.S. Patent 3,732,120, U.S. Patent 3,843,383, U.S. Patent 3,934,070, U.S. Patent 3,481,759, U.S. Patent 3,809,668, U.S. Patent 4,877,767, U.S. Patent 4,857,406, U.S. Patent 4,853,364, U.S. Patent 4,842,981, U.S. Patent 4,842,976, U.S. Patent 4,788,125, U.S. Patent 4,772,532, and U.S. Patent 4,710,570, the disclosures of each of which are totally incorporated herein by reference.

Frequently carbonless paper sets are printed as forms, wherein a large number of sets are printed with standard text or other material, leaving blank areas for individualized information to be filled in by, for example, impact typewriting or handwriting. Typically, carbonless pre-printed forms are generated by techniques such as offset printing. Offset printing and other large scale printing processes, however, require complex and expensive equipment which is not generally found in an office or small business environment. Thus, one desiring forms printed on carbonless paper generally must order them from a professional printer, thus generating added costs and inconvenience, particularly when only a relatively small number of the pre-printed forms are needed. The ability to generate pre-printed carbonless forms on standard office equipment thus can be desirable, particularly when small quantities of forms are desired.

Ink jet printing systems generally are of two types: continuous stream and drop-on-demand. In drop-on-demand systems, a droplet is expelled from an orifice directly to a position on a recording medium in accord-

ance with digital data signals. A droplet is not formed or expelled unless it is to be placed on the recording medium. There are two types of drop-on-demand ink jet systems. One type of drop-on-demand system has as its major components an ink filled channel or passageway having a nozzle on one end and a piezoelectric transducer near the other end to produce pressure pulses. The relatively large size of the transducer prevents close spacing of the nozzles, and physical limitations of the transducer result in low ink drop velocity. Low drop velocity seriously diminishes tolerances for drop velocity variation and directionality, thus impacting the system's ability to produce high quality copies. Drop-on-demand systems which use piezoelectric devices to expel the droplets also suffer the disadvantage of a slow printing speed.

The second type of drop-on-demand system is known as thermal ink jet, or bubble jet, and produces high velocity droplets and allows very close spacing of nozzles. The major components of this type of drop-on-demand system are an ink-filled channel having a nozzle on one end and a heat generating resistor near the nozzle. Printing signals representing digital information originate from an electric current pulse in a resistive layer within each ink passageway near the orifice or nozzle causing the ink in the immediate vicinity to evaporate almost instantaneously and create a bubble. The ink at the orifice is forced out as a propelled droplet as the bubble expands. When the hydrodynamic motion of the ink stops, the process is ready to start all over again.

Ink jet printers of the continuous stream type employ printheads having one or more orifices or nozzles from which continuous streams of ink droplets are emitted and directed toward a recording medium. The stream is perturbed, causing it to break up into droplets at a fixed distance from the orifice. Printing information is transferred to the droplets of each stream by electrodes that charge the passing droplets, which permits each droplet to be individually charged and subsequently positioned by a deflection voltage at a distinct location on the recording medium or sent to the gutter for recirculation. As the droplets proceed in flight from the charging electrodes toward the recording medium, they are passed through an electric field which deflects each individually charged droplet in accordance with its charge magnitude to specific pixel locations on the recording medium. The continuous stream ink jet printing process is described, for example, in U.S. Patent 4,255,754, U.S. Patent 4,698,123 and U.S. Patent 4,751,517, the disclosures of each of which are totally incorporated herein by reference.

Ink jet printers are readily available and are found in business environments in growing numbers. Thus, the ability to print forms on carbonless paper with ink jet printers would enable convenient and inexpensive generation of pre-printed form sets in the office or

business environment.

Most ink jet printers employ aqueous-based inks containing a dye. Printing on conventional carbonless papers with these inks generally results in poor image quality in that image spreading, image bleeding, and slow drying are frequently observed. The present invention enables printing on carbonless paper sets with aqueous-based ink jet inks by modifying the top surface of the color former sheet and/or replacing the conventional color developer coating in known carbonless papers with a coating compatible with the aqueous inks, thus resulting in ink jet prints of high quality and resolution without smearing and with rapid drying times.

Papers coated with materials compatible with ink jet inks are known. For example, U.S. Patent 4,554,181 (Cousin et al.), the disclosure of which is totally incorporated herein by reference, discloses an ink jet recording sheet having a recording surface which includes a combination of a water soluble polyvalent metal salt and a cationic polymer, said polymer having cationic groups which are available in the recording surface for insolubilizing an anionic dye. The recording surface may be formed by applying an aqueous solution of the aforesaid salt and polymer to the surface of an absorbent sheet material such as paper or by applying a coating containing the polymer and salt combination alone or in combination with a binder to the surface of a substrate.

In addition, U.S. Patent 4,792,487 (Schubring et al.), the disclosure of which is totally incorporated herein by reference, discloses an ink jet printing substrate particularly useful as a coating for multi-color, water base ink jet printing. The substrate consists essentially of a high swelling montmorillonite clay and optionally includes a high surface area pigment such as a synthetic silica or calcium carbonate and a water-insoluble binder.

Further, U.S. Patent 4,778,711 (Hosomura et al.), the disclosure of which is totally incorporated herein by reference, discloses an electrophotographic image transfer paper for a copier including a fixing operation which comprises a sheet of raw paper and a receiving layer on the paper for reducing blistering of the sheet during fixing of an image on the sheet. The receiving layer includes a coating on at least one side of the sheet having a center-line-average surface roughness of not more than 2.0 micrometers and an air permeability less than or equal to 4,000 seconds. The coating comprises water soluble adhesives and pigments that have small particle sizes and high levels of oil absorption.

Additionally, U.S. Patent 4,734,336 (Oliver et al.), the disclosure of which is totally incorporated herein by reference, discloses a twin ply uncoated paper for ink jet processes which comprises a supporting paper substrate sheet as a first ply, and thereover as a second ply a paper sheet with filler additives attached to

the fibers thereof. The filler additives are, for example, amorphous synthetic silicas, inorganic silicates, metal alumino-silicates, or inorganic oxides. The patent also discloses three ply papers wherein a supporting substrate first ply is situated between two second plies.

Further, U.S. Patent 4,440,827 (Miyamoto et al.), the disclosure of which is totally incorporated herein by reference, discloses a recording sheet for ink jet recording and optical bar code printing which comprises, on the surface of a support, a coating layer comprising inorganic pigment and an aqueous polymeric binder. The recording sheet is prepared by twice or more repeating a step which comprises coating a coating color prepared by mixing 100 parts by weight of the inorganic pigment containing 50 to 100 parts by weight of synthetic silica with 2 to 18 parts by weight of the aqueous polymeric binder in an amount of 2 to 9 grams (solid) per square meter per one side of the support by one run of coating procedure and then drying the coating color.

In addition, U.S. Patent 4,636,410 (Akiya et al.), the disclosure of which is totally incorporated herein by reference, discloses a recording method of using droplets of a recording liquid wherein the recording surface is formed with at least a filler and part of a fibrous substrate mixed together.

Further U.S. Patent 4,089,547 (Brynko et al.), the disclosure of which is totally incorporated herein by reference, discloses the preparation and application of fumed hydrophilic silica based coatings for manifold paper systems. Receptor sheets treated with the latter coating when used in carbonless pressure sensitive development provide thinner and lighter weight sheets which provide more accurate and more legible replication of hand-written material. The receptor sheet comprises a substrate having deposited thereon a coating comprising hydrophilic fumed silicon dioxide. The particles of silicon dioxide have a surface area of from 200 to 400 square meters per gram.

U.S. Patent 4,906,605 (Kraft), the disclosure of which is totally incorporated herein by reference, discloses a carbonless copy paper for imaging via electrostatic copiers comprising a paper stock having a basis weight greater than about 18 pounds per ream and containing on at least a portion of a surface thereof a stilt particle-free composition comprising microcapsules, at least 50 volume percent thereof having a size no greater than about 12 microns and at least 95 percent by volume thereof having a size no greater than about 18 microns.

In addition, U.S. Patent 4,398,954 (Stolfo), the disclosure of which is totally incorporated herein by reference, discloses a coating composition comprising oil-containing microcapsules dispersed in an aqueous continuous phase, which phase also contains finely divided silica particles and a binder for the microcapsules and silica particles. The silica particles have been treated with an organic material such as an

organic silicon compound to give the particles a hydrophobic surface. The coating composition can be used in the manufacture of paper coated with microcapsules. The paper is characterized by a substantial reduction of specking when used in photocopying apparatuses using a pressure nip to assist transfer of a powder image from a photoreceptor belt to paper. In a preferred embodiment, the coated paper is used in the production of multi-part forms.

U.S. Patent 2,935,438 (Craig), the disclosure of which is totally incorporated by reference, discloses a process for incorporating fillers and pigments into paper. Incorporation of the filler or pigment is intended to impart improved physical and optical properties to the paper, increase the volume or bulk of the paper, impart to the paper opacity, brightness, or color, and result in good surface smoothness, absorption, and ink receptivity of the paper. The process entails reacting precipitated hydrated calcium silicate with aluminum sulfate in an aqueous medium so that at least 50 percent of the calcium silicate is in the solid phase to form a finely divided insoluble reaction product of the calcium silicate and the aluminum sulfate. The insoluble product may then be added to the pulp slurry during manufacture, or it may be later applied to the formed paper sheet.

In addition, U.S. Patent 2,249,118 (De Witt), the disclosure of which is totally incorporated herein by reference, discloses a soft, flexible, durable paper which may be used in the manufacture of articles commonly made of textile fabrics. The paper retains its softness and durability whether wet or dry, and can be cut and sewn like cloth. These characteristics are obtained by incorporating into the paper a sizing material consisting essentially of softening agents, such as glycerine or other stable water soluble liquids with a higher boiling point than water, dissolved in water, and a water insoluble mineral filler, which filler fixes or anchors the softening agent in the paper so that it will not dissolve or evaporate. The filler materials act as adsorbents to retain the softening agent in the paper and distribute it throughout the paper. Suitable fillers include calcium, magnesium, and aluminum oxides, aluminum silicates such as kaolin, fuller's earth, and pumice, and silicates, carbonates, sulfates, and fluorides of calcium and magnesium.

Further, U.S. Patent 4,580,152 (Takigawa et al.), the disclosure of which is totally incorporated herein by reference, discloses a method for carrying out heat sensitive transfer which comprises using a transfer sheet having a leuco dye-containing transfer layer and a receiving sheet having a receiving layer containing a bisphenol-system compound and a porous filler whose oil absorption is 50 ml/100 g or more and bringing the transfer sheet into contact with a thermal head. Examples of porous fillers include inorganic fine powders of silica, aluminum silicate, alumina, aluminum hydroxide, and magnesium hydroxide, and

organic fine powders of urea-formalin resin and styrene resin, with a particle diameter of 0.01 to 10 microns.

Additionally, U.S. Patent 3,801,433 (Windle) discloses a process for reducing the deposition of pitch during paper manufacturing by adding to the pulp from which paper is to be made a quantity of a clay pigment which has been coated with an organic material that adheres strongly to the clay pigment and that renders the surface of the pigment particles oleophilic. The organic material generally is an organic amine, its water-soluble salt, its reaction product with alkylene oxides, an alkyl pyridinium salt, a quaternary ammonium salt, or a mixture thereof, and is applied to the clay pigment in an amount of from 0.5 to 5 percent by weight of the pigment. One suitable clay pigment is kaolinitic clay. The coated pigment is added to the pulp during paper manufacture, and reduces deposition of pitch during manufacture.

U.S. Patent 4,046,404 (Treier), the disclosure of which is totally incorporated herein by reference, discloses a carbonless paper suitable for use in electrostatic copiers the paper comprises a base sheet of paper making fibers having uniformly dispersed therein from about 0.05 to 10 percent by weight of hollow, generally spherical particles ranging in diameter from about 1/2 to 200 microns in diameter. These particles serve the purpose of increasing the stiffness and caliper of the paper sheet. The carbonless paper also contains a color forming material encapsulated in discrete particles and/or a color developing material.

Other references disclosing the use of pigments and clays in paper include U.S. Patent 2,368,635 (Booth), the disclosure of which is totally incorporated herein by reference, which discloses a method of forming a sheet of paper or a ply of paperboard from a dilute suspension of fibers. Preferably, a preformed aluminum silicate mineral is applied to the fiber suspension. The aluminum silicate physically separates the fibers in water so that a more uniform distribution is obtained. In addition, U.S. Patent 2,599,094 (Craig), the disclosure of which is totally incorporated herein by reference, discloses paper containing a cellulosic fiber and calcium silicate pigment. The pigment comprises highly pigmented cellulosic pulp fibers containing finely divided hydrated calcium silicate precipitated largely within the fibers and on and around the fibers in an amount greatly exceeding the weight of the fibers. Further, U.S. Patent 2,786,757 (Taylor), the disclosure of which is totally incorporated herein by reference, discloses a process for preparing a paper product with high brightness and opacity by forming a paper pulp dispersion in an aqueous acidic material which forms a substantially water-insoluble salt of an alkaline earth metal and adding calcium silicate or an equivalent alkaline earth metal silicate to the acidic slurry. U.S. Patent 2,786,758 (Taylor), the disclosure of which is totally incorporated herein by

reference, discloses a process for preparing paper containing a siliceous pigment. The pigment is prepared by reaction of an alkaline earth metal silicate such as calcium silicate with aluminum sulfate in an aqueous medium initially containing an alkaline earth metal sulfate such as calcium sulfate. Paper of high whiteness and brightness is prepared by adding to a slurry of paper forming fibers a quantity of aluminum sulfate and, after the aluminum sulfate solution has permeated the pores of the slurry, adding a quantity of calcium silicate. Additionally, U.S. Patent 2,888,377 (Allen), the disclosure of which is totally incorporated herein by reference, discloses a process for producing calcium silicate, which can be used as an opacifier, reinforcing pigment, or loading agent for paper. Further, U.S. Patent 2,919,222 (Hall, Jr.), the disclosure of which is totally incorporated herein by reference, discloses a process for making paper wherein finely divided, hydrated calcium silicate pigment is added to a furnish comprising pulp, sizing material, filler, and other ingredients to form paper containing the pigment.

U.S. Patent 4,478,910 (Oshima et al.), the disclosure of which is totally incorporated herein by reference, describes the application of various high surface area pigment-based formulations to base papers with a specific degree of hydrophobic sizing, to produce highly absorbent recording papers with more plain-paper like tactile properties. U.S. Patent 4,154,462 (Golden et al.), the disclosure of which is totally incorporated herein by reference, discloses a transfer sheet having a substrate coated with pressure-rupturable microcapsules containing an oil and an oil-soluble dye intermediate and a particulate oil-absorptive material which is non-reactive with the dye intermediate and is situated with respect to the microcapsules such that oil released by the microcapsules is absorbed thereby. The concentration of oil absorptive material is sufficient to permit writing on the coated substrate without interference from oil released by ruptured microcapsules but less than that which material reduces the transfer of oily solution from ruptured microcapsules to an underlying copy sheet. Also, U.S. Patent 3,481,759 (Ostlie), the disclosure of which is totally incorporated herein by reference, discloses self-marking papers of the transfer or manifolding type that operate by having a dye precursor within microscopic capsules carried as a transfer coating on one sheet of paper, the dye precursor within the capsules reacting with a receptor coating on a mating sheet of paper to produce a visible mark on the mating sheet upon impact against the contacting transfer and receptor coatings when the two sheets of paper are mated, the microcapsules at the point of impact rupturing and releasing their contents onto the receptor coating of the mating sheet. To prevent the inadvertent marking or backgrounding during handling, a co-reactant for the dye precursor is included in

the transfer coating containing the capsules but externally of the capsules so that upon the inadvertent rupture of capsules in the transfer coating the contents will react with the colorless co-reactant before passage through the sheet or transfer to the receptor sheet coating, and thus prevent inadvertent marking of the paper. Scuff capsules to help further prevent inadvertent marking may also be included in the transfer coating along with the dye precursor containing capsules. Further, U.S. Patent 4,089,547 (Brynko et al.), the disclosure of which is totally incorporated herein by reference, discloses manifold receptor sheets for use with conventional donor sheets, the receptor sheet comprising a substrate having deposited thereon a coating comprising hydrophobic fumed silicon dioxide, together with processes for producing such receptor sheets. The reference discloses a carbonless color developer coating consisting of very small particles (7 to 14 nanometers in diameter) of hydrophobic fumed silica and a suitable binder.

Of additional background interest are U.S. Patent 2,929,736 (Miller et al.), which discloses a heat and pressure responsive record material in which a micro-encapsulated color former solution and a color developing pigment are combined in a single coating; U.S. Patent 2,980,941 (Miller), which discloses a soil-removing sheet consisting of encapsulated soil-removing solvent along with an absorptive material such as Fuller's earth; and U.S. Patent 3,776,864 (Woerner), which discloses a transfer ink containing a dye and a filler to prevent the coating from having a greasy surface.

Although the known compositions and processes are suitable for their intended purposes, a need remains for a carbonless paper that is suitable for use in ink jet printers. In addition, a need exists for printing processes that enable generation of pre-printed carbonless forms on commonly available office equipment. Further, there is a need for carbonless paper compatible with aqueous ink jet inks. There is also a need for carbonless paper that can be printed with aqueous ink jet inks wherein the images exhibit high quality resolution, rapid drying times, and permanence to water.

It is an object of the present invention to provide a carbonless paper and a printing process which strive to meet the above needs.

Accordingly, there is provided a process for generating images which comprises incorporating into an ink jet printing apparatus a carbonless paper set which comprises a first sheet comprising a support containing a color developer capable of reacting with a color former to produce a color image, and a second sheet comprising a support coated with the color former, characterised in that said co/or developer comprises high surface area silica particles, and forming an image on the first sheet by causing ink to be expelled in droplets on a surface containing the color

developer, and forming an image on the second sheet by causing ink to be expelled in droplets onto the surface opposite to that coated with the color former. The second sheet can also optionally be further modified on the surface not coated with the color former with a suitable treatment for optimizing its ink jet print quality. In another embodiment of the invention, the carbonless paper set also contains one or more intermediate sheets of paper containing on one surface a color developer comprising high surface area silica particles and on the opposite surface with a color former. When one or more additional intermediate sheets are present, the process also includes the steps of forming images on the intermediate sheets by causing ink to be expelled in droplets on the surface containing the color developer.

The present invention also provides a carbonless paper set including a first sheet comprising a support containing a color developer capable of reacting with a color former to produce a color image, and a second sheet comprising a support coated with the color former, characterised in that said color developer comprises high surface area silica particles, and said first and second sheets are arranged such that, when incorporated into an ink jet printing apparatus, an image can be formed on the first sheet by causing ink to be expelled in droplets on a surface containing the color developer, and an image can be formed on the second sheet by causing ink to be expelled in droplets onto the surface opposite to that coated with the color former.

In a preferred embodiment there is provided a carbonless paper set which comprises a first sheet comprising a support containing a color developer capable of reacting with a color former to produce a color image, and a second sheet comprising a support coated with the color former, characterised in that said color developer comprises silica particles having a surface area of from about 100 to about 195 square meters per gram.

The carbonless paper sets employed in the processes of the present invention comprise at least two sheets of base paper, each of which contains on one surface either a color former or a color developer. Optional intermediate sheets are coated on one surface with a color former coating and on the other surface with a color developer coating. The support or base paper may comprise pulp fibers and blends thereof originating from bleached hardwood and softwood fibers, bleached mechanical pulp fibers, cotton fibers, and synthetic fibers. More specifically, examples of suitable cellulosic pulps include Domtar Seagul W and Q90, a 75/25 percent bleached hardwood and softwood blend of fibers, and 100% bleached groundwood pulp (Acadia Forest Products Ltd.). Formed sheets derived from cellulosic pulps should be suitably sized so as to minimize penetration of subsequent coating material. Internal and surface

sizing treatments include, for example, rosin acid/alum, alkyl ketene dimer, starch, and/or various synthetic polymers.

The color formers generally comprise a binder plus microcapsules containing a color forming material dissolved in a suitable solvent. In general, the color forming material can be either a substantially colorless basic dye precursor, or an organic complexing agent, or a combination of the two. The color forming material may be a colorless basic dye precursor such as, for example, benzoyl leuco methylene blue; diaryl phthalides such as 3,3-bis (4-dimethylaminophenyl)-6-dimethylaminophthalide (Crystal Violet Lactone) and 3,3-bis (4-dimethylaminophenyl) phthalide (Malachite Green Lactone); other phenyl-, indolpyrrol-, and carbazol- substituted phthalides; leucauramines; acyl auramines; unsaturated aryl ketones; basic mono azo dyes; Rhodamine B Lactams; polyaryl carbinols; nitro-, amino-, amido-, sulfon amido-, aminobenzylidene-, halo-, and anilino- substituted fluorans, such as 3-diethylamino-6-methyl-7-anilino-fluoran; spirodipyrans; pyridine and pyrazine compounds; or the like. Examples of a colorless basic dye precursor are disclosed in U.S. Patent 2,417,897, U.S. Patent 3,672,935, U.S. Patent 3,681,390, U.S. Patent 4,202,820, and U.S. Patent 4,675,706, the disclosures of which are totally incorporated herein by reference. The color forming material may also be an organic complexing agent. Examples of organic complexing agents include those listed in U.S. Patent 3,481,759, U.S. Patent 4,334,015, and U.S. Patent 4,372,582, the disclosures of which are totally incorporated herein by reference. Examples of organic complexing agents include dithiooxamide and its derivatives such as N,N'-di-benzyl-dithiooxamide, N,N'-bis(2-octanlyloxyethyl) dithiooxamide, and di-dodecyl dithiooxamide; aromatic substituted hydrazones such as those disclosed in U.S. Patent 4,334,015; or the like.

Typically the chosen color former material, or combination of color former materials, is dissolved in a suitable organic solvent and encapsulated in a hard polymeric shell by one of several known encapsulation techniques. Examples of suitable solvents include alkyl biphenyls such as propylbiphenyl and butylbiphenyl; dialkyl phthalates such as diethylphthalate, dibutylphthalate, dioctylphthalate, dinonylphthalate, and ditridecylphthalate; alkylated naphthalenes such as dipropyl-naphthalene; C₁₀ - C₁₄ alkyl benzenes such as dodecyl benzene; alkyl or aralkyl benzoates such as benzyl benzoate; benzylxylene; benzylbutylphthalate; ethyldiphenylmethane; 2,2,4-trimethyl-1,3-pentanediol diisobutyrate; partially hydrogenated terphenyls; cyclohexane; toluene; 3-heptanone; tributyl phosphate; and mixtures of the above. The solvents for the color former can include any of the above which possess sufficient solubility for the color former. A suitable solvent

should be capable of dissolving at least about 1 percent by weight and preferably from about 2 to about 10 percent by weight of the color former. In the case of a basic dye precursor/acidic polymer developer system, or an organic complexing agent/transition metal salt system, the color former solvent preferably is also a cosolvent for the color developer material to promote the color forming reaction. Of course, a suitable solvent must also be a non-solvent for the chosen microcapsule wall material.

Minute droplets of color former solution are produced by emulsifying the solvent oil in an aqueous medium. The color former solution droplets can then be encapsulated in a polymeric shell by any one of a number of known microencapsulation techniques, such as coacervation, complex coacervation, interfacial polymerization, in-situ polymerization, or the like. Methods for encapsulating minute droplets of color former solution in a polymeric shell are described in, for example, U.S. Patent 2,800,457, U.S. Patent 2,800,458, U.S. Patent 3,418,250, and U.S. Patent 3,516,941, the disclosures of each of which are totally incorporated herein by reference. Capsule wall forming materials include but are not limited to gelatin wall formers such as gum arabic, polyvinyl alcohol, and carboxymethylcellulose; isocyanate wall-formers; urea-formaldehyde and urea-resorcinol-formaldehyde; melamine-formaldehyde; polyurea; polyurethane; polyamide; polyester; and the like. The completed microcapsules are typically from about 1 to about 50 microns and preferably from about 5 to about 10 microns in diameter. The capsule fill of color former in solvent typically comprises from about 50 to about 95 percent of the total capsule weight.

A coating formulation is prepared by mixing an aqueous dispersion of microcapsules containing color former solution with an aqueous dispersion of a suitable binder, such as starch, polyvinyl alcohol, latex, or the like with a capsule:binder ratio typically being from about 9:1 to about 7:3. The capsule plus binder dispersion is then coated onto a paper support using any one of a number of known paper coating techniques, such as roll, gravure, air-knife, blade, rod, or slot die coating, although methods that minimize capsule breakage, such as roll and air-knife, are preferred.

Optionally, the color former coating can also include from about 5 to about 10 percent by weight of particles of somewhat larger size than the microcapsules. For example, as disclosed in U.S. Patent 4,630,079, the disclosure of which is totally incorporated herein by reference, the color former coating contains particles of somewhat larger size than the microcapsules to prevent or reduce accidental or premature breakage of the microcapsules. Such particles typically comprise fine powders of cellulose, starch granules, or various types of plastic beads. Dry coat weights for the color former coating typically range from about 2 to about 10 grams per square

meter, which typically includes from about 1 to about 5 grams per meter of solvent and from about 0.01 to about 0.1 grams per square meter of color former.

When present as a coating, the color developers generally comprise high surface area silica particles dispersed in a water-soluble binder. Any water-soluble binder material can be employed, such as those commonly employed in coatings for ink jet papers or transparencies. Examples of suitable binders include but are not limited to polyvinyl alcohol, such as VINOL 350 available from Air Products and carboxymethyl cellulose available from Hercules, and the like as well as mixtures thereof. An additional binder material or materials in the coating compositions for the papers of the present invention, when present in combination with the pigment and polyvinyl alcohol, can impart to the paper improvements in characteristics such as surface friction, optical density, adhesion of the coating to the paper, reduced chalking, a more plain-paper like feel, waterfastness, and uniform solid area colors. The additional binder can be a styrene-butadiene latex, a cationic polyamine, a styrene-vinyl pyrrolidone copolymer, a styrene-maleic anhydride copolymer, a polyvinyl pyrrolidone, or a vinyl pyrrolidone-vinyl acetate copolymer, and can also constitute a mixture of two or more of these materials. If desired, additional additives can be incorporated into the color developer coating provided that these additives do not interfere with development of an image upon rupture of the color former material.

The high surface area silica particles provide a surface compatible with aqueous ink jet inks, in contrast to the low surface area clays (i.e., less than 25 square meters per gram) conventionally employed in carbonless paper color developer coatings. The surface area of the silica particles is high enough to provide effective absorption of ink upon contact with the coated paper. Generally, the particles have a surface area of at least about 100 square meters per gram, and preferably at least from about 100 to about 195 square meters per gram, and the surface area typically ranges from about 150 to about 375 square meters per gram, preferably from about 250 to about 375 square meters per gram, although the surface area can be outside of this range. Examples of suitable silica particles include synthetic amorphous colloidal silica such as Syloid 74 available from Grace-Davison Company, calcium silicates inclusive of XP974 available from Huber Corporation, and sodium aluminium silicates such as Zeolex 80 available from Huber Corporation, and synthetic precipitated silica such as Zeo and Zeothix 265 available from Huber Corporation. The particles are present in the binder in an effective amount, typically from about 50 to about 90 percent by weight, and preferably from about 60 to about 80 percent by weight, although the amount can be outside of this range.

The coating formulation is prepared by pre-dis-

persing the silica in water, then adding preheated binder, adjusting the pH, and finally incorporating additional binder material or materials and other additive such as surfactants.

The color developer coating is applied to a suitable base paper either by a laboratory draw-down method using wire wound rods or on a pilot coating machine equipped with a reverse-roll coating station and dried with a hot-air dryer. The color developer coating can be present in any effective coating thickness. Typical coating thicknesses are from about 5 to about 25 microns, and preferably from about 10 to about 20 microns, although the coating thickness can be outside of this range.

The color developer sheet can also contain high surface area silica particles dispersed among the pulp fibers instead of in a distinct coating. Papers of this kind can be prepared by any suitable process, such as that described in U.S. Patent 4,734,336, the disclosure of which is totally incorporated herein by reference. In this instance, another embodiment of the present invention relates to a twin ply uncoated paper for ink jet processes which comprises a supporting paper substrate sheet as a first ply in a thickness of 50 to 90 microns, and thereover as a second ply a paper sheet with a thickness of from about 5 to about 50 microns and filler additives, for example from about 25 to 75 percent by weight, attached to the fibers thereof, which additives are selected from the group consisting of synthetic silicas, inorganic silicas, such as sodium aluminosilicates, and inorganic oxides yielding a composite sheet with excellent drying, high image resolution, that is for example images with high edge definition, and wherein the aforementioned sheet also possesses excellent waterfastness with certain colored aqueous anionic dye-based ink jet compositions.

Optionally, the surface of the first sheet in the set, which is coated on one surface with the color former, can be coated on the other surface with the color developer coating comprising a water-soluble binder material and high surface area silica particles to enhance the affinity of the paper surface for aqueous ink jet inks and to improve image quality. Alternatively, this surface can remain uncoated or can be treated by any other desired method to enhance the quality of ink jet images generated thereon.

Conventional carbonless paper technology typically employs one of two approaches. In the first, the color former is a colorless precursor dye which becomes colored upon contact with the relatively acidic surface of the color developer. One example of a commercially available carbonless paper employing this approach is the NCR brand of carbonless paper manufactured by Appleton Papers Inc., Appleton, WI. Recording sheets of the present invention are suitable for this type of development. High surface area silica, although typically referred to as SiO_2 , also contains

water physically sorbed or chemisorbed onto the surface. This bound water, generally represented by the silanol group Si-OH, displays considerable acidic properties. Thus, the silica particles impart to the color developer coating the acidic nature that will result in development of color images when the precursor dye contacts the developer surface.

In the second approach, the color former is a colorless material that forms a colored metal complex upon contacting the color developer surface. One example of a commercially available carbonless paper employing this approach is 3M Tartan, available from the Minnesota Mining and Manufacturing Company, St. Paul, MN. Recording sheets of the present invention can be rendered suitable for this type of development by treating the development surface with an organic complexing agent color developer which generally comprises a salt of a transition metal such as Ni, Cu, Co, or Zn. Examples of transition metal salts for color developers include nickel 2-ethylhexoate and nickel rosinate. A color developer sheet may be produced by adding to the initial paper pulp slurry a water soluble rosin salt such as sodium rosinate, along with a water soluble metal salt such as nickel sulfate, which causes an insoluble metal rosinate, i.e. nickel rosinate, to be precipitated as a sizing on the paper fibers. The treated fibers are then formed into a paper sheet by conventional papermaking techniques. Alternately, an aqueous dispersion of nickel rosinate combined with an inorganic pigment such as silica and a suitable binder may be coated on the surface of a paper support by any of a number of known techniques.

Specific embodiments of the invention will now be described in detail. These examples are intended to be illustrative, and the invention is not limited to the materials, conditions, or process parameters set forth in these embodiments. All parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

A color developer coating formulation was prepared for which the solids portion contained 74.3 percent by weight high surface area silica particles (Syloid 74, available from Grace-Davison Chemical Division, having a surface area of 340 square meters per gram), 12.0 percent by weight of polyvinyl alcohol (Vinol 350, available from Air Products), 0.5 percent by weight of a cationic polyamine (Cypro 514, available from American Cyanamid), 10.0 percent by weight of a carboxylated styrene-butadiene latex co-binder (Polysar 478, available from Polysar Limited), 1.0 percent by weight of a non-ionic surfactant (Triton X 100, available from Rohm and Haas), and 1.0 percent by weight of sodium hydroxide to adjust the pH of the formulation to 8.0. Coating formulations comprising about 18 percent by weight solids were prepared

by pre-dispersing the silica particles in water to de-aerate fully. Polyvinyl alcohol that had previously been heated at 95°C for about 1 hour was then added and the pH was adjusted to 8.0 with the sodium hydroxide. Subsequently, the cationic polyamine was added, followed by the styrenebutadiene latex and thereafter the surfactant. All of these process steps took place at or near ambient room temperature and pressure. The viscosity of the coating formulations was from about 100 to about 150 centipoise as measured using a Brookfield LVF Type Viscometer, Brookfield Engineering Labs, Stoughton, MA and Spindle #2 at 60 rpm. The coatings were then applied to a heavily sized diazo base paper of basis weight 71.5 g/m² (available from Domtar Inc.) by draw-down coating techniques with a Meyer rod #22 to form coated papers with a coating weight of from about 8 to about 10 grams per square meter. The coatings were dried with a hot-air gun at about 100°C for 1 minute.

EXAMPLE II

Another color developer coating was prepared as described in Example I with the exception that the cationic polyamine Cypro 514 was present in an amount of 7 percent by weight and the silica Syloid 74 was present in an amount of 69 percent by weight; the proportion of the other ingredient remained the same. This coating was manufactured on a coating machine (Faustel Inc., Germantown, WI) operating with a reverse roll assembly at 3 feet per minute, and provided a waterfast surface treatment compatible with anionic dye-based ink jet inks.

EXAMPLE III

A twin ply paper was prepared according to the method disclosed in U.S. Patent 4,734,336, the disclosure of which is totally incorporated herein by reference, as follows.

The base sheet comprised a fine paper furnish containing a 75/25 percent bleached hardwood (Domtar Seagul 'W') and softwood fibers (Domtar Q90) beaten to a Canadian Standard Freeness value of approximately 400 to 450; and the second ply comprised the same furnish blended with the high surface area colloidal silica pigment filler, Syloid 74, available from Grace-Davison. More specifically a first pulp suspension for the base ply was supplied from stock tank A at 0.4 percent consistency to produce a base sheet of 65 grams per square meter basis weight onto a forming wire via a vertically-oscillating nozzle. The second agitated pulp suspension (stock tank B) containing a blend of pulp and 50 percent silica filler was applied to the first pre-formed ply (which was maintained as a wet fiber slurry on the wire) by an oscillating nozzle, and then drained to form a paper structure

with two discrete plies having total basis weight of about 75 grams/meters². The thickness of the base or second ply may accordingly be varied by increasing the number of nozzle passes. In this example the number of nozzle passes was computed so as to result in twin ply sheet with a top ply 14 percent of the total sheet thickness. After draining the sheet to about 20 percent dryness, that is a level at which it possessed adequate wet strength, the sheet was stripped from the wire, further de-watered on a single nip wet press with the second (top) ply sandwiched against a smooth Teflon surface and the base ply against a press felt, and then dried on a photographic-type drum dryer. The thickness of the first and second plies together was about 100 microns.

EXAMPLE IV

Four carbonless paper sets were prepared and imaged as follows. One set of NCR carbonless paper, available from Appleton Papers Inc., Appleton, WI, comprised a first sheet (having a color former coated onto the surface opposite to that upon which images are to be formed) and a second sheet (having a color developer coated onto the surface upon which images are to be formed). Both sheets were incorporated into an IBM Selectric typewriter situated so that the color former coating of the first sheet was in contact with the color developer coating of the second sheet. Images were formed on the first sheet by typing onto the surface opposite to that having the color former coating. Corresponding images were formed on the surface of the second sheet coated with the color developer.

Three additional sets of NCR brand carbonless paper were disassembled and the second sheet of each was replaced with, respectively, the recording sheets prepared as described in Examples I, II, and III, with new carbonless sets being assembled so that the color developer coating of the second sheets contacted the color former coatings of the first sheets. Each of these sets were incorporated into an IBM Selectric typewriter situated so that the color former coating of the first sheet was in contact with the color developer coating of the second sheet. Images were formed on the first sheet by typing onto the surface opposite to that having the color former coating. Corresponding images were formed on the surface of the second sheet coated with the color developer.

The images formed on the recording sheet of Example I exhibited edge acuity comparable to the images obtained with the carbonless set having the NCR color developer sheet and exhibited an improved optical density compared to that obtained with the carbonless set having the NCR color developer sheet. The images formed on the recording sheets of Examples II and III exhibited edge acuity and optical density comparable to the images obtained with the carbonless set having the NCR

color developer sheet. In all instances, carbonless image development was virtually instantaneous.

EXAMPLE V

The ink jet print quality performance of the carbonless sets described in Example IV was assessed in an HP Deskjet® black ink printer and a Xerox® 4020 color printer. Text and solid area black images printed with the HP Deskjet® printer on the color developer sheets prepared as described in Examples I, II and III had noticeably superior optical density, solid area uniformity and edge acuity compared with the NCR color developer sheet. Similarly a primary and secondary color checker board pattern of colored inks printed with a Xerox® 4020 printer on the color developer sheets prepared as described in Examples I, II and III produced more vibrant solid area color images, with no inter-color bleed and highly uniform optical densities compared with images printed on the NCR color developer sheet which appeared much duller, exhibited inter-color bleed and were highly mottled.

EXAMPLE VI

Two recording sheets as described in Example II were dip coated in aqueous nickel chloride solutions, with the first sheet being dipped in a 1% solution (sheet VIa) and the second sheet being dipped in a 5% solution (sheet VIb).

Three carbonless paper sets were then prepared and imaged as follows. One set of 3M Tartan carbonless paper, available from the Minnesota Mining and Manufacturing to., St Paul, MN comprising a first sheet (having a color former coated onto the surface opposite to that upon which images are to be formed) and a second sheet (having a color developer coated onto the surface upon which images are to be formed). Both sheets were incorporated into an IBM Selectric typewriter situated so that the color former coating of the first sheet was in contact with the color developer coating of the second sheet. Images were formed on the first sheet by typing onto the surface opposite to that having the color former coating. Corresponding images were formed on the surface of the second sheet coated with the color developer.

Two additional sets of 3M Tartan carbonless paper were disassembled and the second sheet of each was replaced with sheets VIa and VIb, respectively, with new carbonless sets being assembled so that the color developer coating of the second sheets contacted the color former coatings of the first sheets. Each of these sets were incorporated into an IBM Selectric typewriter situated so that the color former coating of the first sheet was in contact with the color developer coating of the second sheet. Images were formed on the first sheet by typing onto the surface

opposite to that having the color former coating. Corresponding images were formed on the surface of the second sheet coated with the color developer.

The images obtained on sheets VIa and VIb each formed images comparable in quality to the images obtained with the carbonless set having the 3M Tartan color developer sheet, with the images formed on sheets VIa and VIb being somewhat broader and more reddish-violet in color compared with the bluish-violet images obtained on the 3M Tartan color developer sheet. The rate of carbonless image development was fastest for the set containing the 3M Tartan color developer sheet, with the rate being somewhat slower for the set containing color developer sheet VIb and significantly slower for the set containing color-developer sheet VIa. These development rates suggest that the absorbent silica coatings in sheets VIa and VIb diminished the effective concentration of Ni^{2+} for complexation with the colorformer composition as compared to the relatively less absorbent clay coating on the 3M Tartan developer coating. Images formed on sheets VIa and VIb were very clean and withstood background pressure development during transfer through the typewriter feed rolls, whereas the carbonless set containing the 3M Tartan color developer sheet exhibited very noticeable background development.

EXAMPLE VII

The ink jet print quality performance of the carbonless sets described in Example VI were evaluated on a HP Deskjet® printer and Xerox® 4020 color printer. The color developer sheets printed with the HP Deskjet® printer, examples VIa and VIb, had noticeably superior optical density, solid area uniformity and edge acuity compared with the 3M color developer sheet. Similarly Xerox® 4020 color prints on examples VIa and VIb produced more vibrant solid area color images with no inter-color bleed and highly uniform optical density compared with images printed on the 3M color developer sheet which appeared much duller, had noticeable inter-color bleed and highly mottled solid areas.

Other embodiments and modifications of the present invention may occur to those skilled in the art subsequent to a review of the information presented herein; these embodiments and modifications, as well as equivalents thereof, are also included within the scope of this invention.

Claims

1. A process for generating images which comprises incorporating into an ink jet printing apparatus a carbonless paper set which comprises a first sheet comprising a support contain-

ing a color developer capable of reacting with a color former to produce a color image, and a second sheet comprising a support coated with the color former, characterised in that said color developer comprises high surface area silica particles, and forming an image on the first sheet by causing ink to be expelled in droplets on a surface containing the color developer; and forming an image on the second sheet by causing ink to be expelled in droplets onto the surface opposite to that coated with the color former.

2. A process as claimed in claim 1, characterised in that the carbonless paper set also contains at least one intermediate sheet comprising a support coated on one surface with a color former and containing on the other surface a color developer comprising high surface area silica particles, and wherein an image is formed on each intermediate sheet by causing ink to be expelled in droplets onto the surface opposite to that coated with the color former.
3. A carbonless paper set including a first sheet comprising a support containing a color developer capable of reacting with a color former to produce a color image, and a second sheet comprising a support coated with the color former, characterised in that said color developer comprises high surface area silica particles, and said first and second sheets are arranged such that, when incorporated into an ink jet printing apparatus, an image can be formed on the first sheet by causing ink to be expelled in droplets on a surface containing the color developer, and an image can be formed on the second sheet by causing ink to be expelled in droplets onto the surface opposite to that coated with the color former.
4. A carbonless paper set which comprises a first sheet comprising a support containing a color developer capable of reacting with a color former to produce a color image, and a second sheet comprising a support coated with the color former, characterised in that said color developer comprises silica particles having a surface area of from about 100 to about 195 square meters per gram.
5. A carbonless paper set as claimed in claim 3 or claim 4, characterised in that the color developer is a coating on the surface of the support which comprises the silica particles in a water soluble polymeric binder.
6. A carbonless paper set as claimed in claim 5, characterised in that the binder is selected from the group consisting of polyvinyl alcohol, car-

boxymethyl cellulose, and mixtures thereof.

7. A carbonless paper as claimed in claim 6, characterised in that the binder also contains a component selected from the group consisting of styrene-butadiene latices, cationic polyamine, a styrene-vinyl pyrrolidone copolymer, styrene-maleic anhydride copolymer, polyvinyl pyrrolidones, vinyl pyrrolidone-vinyl acetate copolymers and mixtures thereof. 5 10
8. A carbonless paper set as claimed in any one of claims 3 to 7, characterised in that the first sheet comprises a twin ply paper having a supporting paper substrate sheet as a first ply, and thereover as a second ply a paper sheet with high surface area silica particles attached to the fibers thereof. 15
9. A carbonless paper set as claimed in claim 8, characterised in that the silica particles are present in the second ply in an amount of from about 25 to about 75 percent by weight. 20
10. A carbonless paper set as claimed in claim 8 or claim 9, characterised in that the first ply has a thickness of from about 50 to about 90 microns and the second ply has a thickness of from about 5 to about 50 microns. 25
11. A carbonless paper set as claimed in any one of claims 8 to 10, characterised in that the silica particles have a surface area of at least about 100 square meters per gram. 30
12. A carbonless paper set as claimed in any one of claims 3 to 11, characterised in that the first sheet also contains a transition metal salt. 35
13. A carbonless paper set as claimed in claim 12, characterised in that the transition metal salt is selected from the group consisting of nickel 2-ethylhexoate and nickel rosinat. 40
14. A process as claimed in claim 1 or claim 2, characterised in that the carbonless paper set used is as claimed in any one of claims 3 to 13. 45
15. A process as claimed in claim 14, characterised in that the coating is present on the paper in a thickness of from about 5 to about 25 microns. 50
16. A process as claimed in claim 15, characterised in that the coating contains silica particles in an amount of from about 50 to about 90 percent by weight. 55
17. A process as claimed in any one of claims 1, 2 or 14 to 16, characterised in that the silica particles

have a surface area selected from a group of ranges consisting of from about 100 to about 195 square meters per gram, from about 150 to about 375 square meters per gram, from about 250 to about 375 square meters per gram.



European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 91 31 0758

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A, D	US-A-4 089 547 (C. BRYNKO ET AL.) * column 2, line 21 - line 35 * ----	1-17	B41M5/155 B41M5/00 B41M5/124 B41M1/36
A	US-A-3 020 171 (J. A. BAKAN) * column 1, line 1 - line 55 * ----	1-17	
A	EP-A-0 162 930 (MATSUSHITA ELECTRIC INDUSTRIAL COMPANY LIMITED) * page 3, line 10 - line 14 * * page 4, line 4 - line 8; claim 1 * ----	1-17	
A	EP-A-0 022 875 (MISHIMA PAPER COMPANY LIMITED) * the whole document * -----	1-17	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B41M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 FEBRUARY 1992	Examiner BACON A. J.
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			

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