



EUROPEAN PATENT APPLICATION

Application number : **94400803.6**

Int. Cl.⁵ : **B41M 5/124**

Date of filing : **13.04.94**

Priority : **15.04.93 US 47848**

Date of publication of application :
19.10.94 Bulletin 94/42

Designated Contracting States :
DE FR GB

Applicant : **MINNESOTA MINING AND
MANUFACTURING COMPANY**
3M Center,
P.O. Box 33427
St. Paul, Minnesota 55133-3427 (US)

Inventor : **Kraft, Keith A., c/o Minnesota Mining
and
Manufact. Co.,
2501 Hudson Road,
P.O. Box 33427
St. Paul, Minnesota 55133-3427 (US)**
Inventor : **Stolte, Roger L., c/o Minnesota
Mining and
Manufact. Co.,
2501 Hudson Road,
P.O. Box 33427
St. Paul, Minnesota 55133-3427 (US)**

Representative : **Ahner, Francis et al**
CABINET REGIMBEAU
26, avenue Kléber
F-75116 Paris (FR)

Legume starch stiltling material for carbonless papers used in offset printing presses and in copier/duplicators.

The incorporation of refined legume starch granules, and particularly pea starch granules, into carbonless paper coatings, preferably CB (coated back) coatings, provides an unexpected improvement in smudge and scuff resistance when compared to the use of other commonly used stilt materials such as wheat starch. The incorporation of refined legume starch granules reduces press and copier contamination and provides a cleaner printed sheet when printed on offset printing presses, electrophotographic and electrophotographic copier/duplicators, and laser printers.

BACKGROUND OF THE INVENTION

Field of Invention

5 This invention relates to carbonless papers incorporating refined legume starch as a stiling material into the CB (coated back) coatings. Carbonless papers incorporating refined legume starch are particularly useful when used in high speed electrophotographic copier/duplicators, offset printing presses, and laser printers. Carbonless papers incorporating refined legume starch as a stiling material are less prone to capsule rupture during printing operations and less prone to feeder induced smudging when compared with carbonless papers
10 employing the traditionally used wheat starch.

Description of Related Art

Carbonless impact marking papers for the transfer of images, (i.e., carbonless copy papers) are papers
15 which are capable of producing an image upon application of pressure. Products employing this chemistry generally comprise at least two substrates (for example, two sheets of paper) and involve coating one reactant, known as a color-former, on one substrate, and the other reactant, known as a developer, on another "mating" substrate. One surface, or side, of each substrate is coated with one of the two primary reactants. The two substrates are often referred to as a donor sheet and a receptor sheet. Means for preventing the reacting of
20 the two until intended (i.e., until activating pressure is applied) are also provided. This is typically accomplished by encapsulation of one of the reactants. Preferably, a fill solution of the color-forming compound(s) in a hydrophobic solvent is encapsulated or contained in microcapsules and is coated on the back side of one sheet of paper to form a donor sheet. This donor sheet is then mated with a receptor sheet coated with a developer or reactant for the color-forming compound. The microcapsules serve the purpose of isolating the reactants
25 from one another and preventing reaction. Once activating pressure is applied to the uncoated surface of the donor sheet, such as from a stylus (such as a pencil or pen) or business-machine key (such as a typewriter or impact printer), the two substrates come into contact under sufficient pressure so that the capsules rupture (i.e., those capsules corresponding to the pattern of applied pressure) and the solution of encapsulated color-former is released and transferred from the donor sheet to the receptor sheet. On the receptor sheet, a reaction
30 between the previously separated reactants occurs. Since the color-former and the developer form a deeply colored image when reacted, an image forms on the receptor sheet. In general, the resulting reaction will, of course, form a colored image corresponding to the path traveled by the stylus or the pattern of pressure provided by the stylus or key. The term "activating pressure" includes, but is not limited to, pressure applied by hand with a stylus or pressure applied by a business machine key (for example, a typewriter key); and the term
35 "encapsulation" and "encapsulated compounds" refer to microcapsules enclosing a fill material.

The chemistry used in carbonless papers is of two general types. In one type of carbonless paper, the image results from the reaction between an encapsulated leuco dye color-former and an acid, a phenolic, or acidic clay developer. In another type of carbonless paper, the image results from the formation of a colored coordination compound by the reaction between an encapsulated ligand color-former and a transition metal
40 developer.

A preferred construction contains an encapsulated color-former dissolved in appropriate hydrophobic solvent(s) within microcapsules and coated with a suitable binder onto a back side of the donor sheet, sometimes referred to as a "coated back" (CB) sheet. A developer, also optionally in a suitable binder such as a starch or latex, is coated onto the front side of the receptor sheet sometimes referred to as a "coated front" (CF) sheet.
45 The term "suitable binder" refers to a material, such as starch or latex, that allows for dispersion of the reactants in a coating on a substrate. Each CB coating contains rupturable capsules which, when ruptured, release reagents to produce a color-changing reaction at the adjacent CF coating. The preparation of such carbonless sheets is disclosed by Gale W. Matson in U.S. Patent Nos. 3,516,846 and 3,516,941, the disclosures of which are incorporated herein by reference.

50 A wide variety of processes exist by which microcapsules can be manufactured and a wide variety of capsule materials can be used in making the capsule shells, including gelatin and synthetic polymeric materials. A popular material for shell formation is the product of the polymerization reaction between urea and formaldehyde (UF capsules), or between melamine and formaldehyde (MF capsules), or the polycondensation products of monomeric or low molecular weight polymers of dimethylolurea or methylolated urea with aldehydes.

55 As stated previously, in imaging, the two sheets are positioned such that the back side of the donor sheet faces the developer coating on the front side of the receptor sheet. In many applications the uncoated surface of the donor (CB) sheet contains a form of some type and the activating pressure is generated by means of a pen or other writing instrument used in filling out the form. Thus, the image appearing on the receptor (CF)

sheet is a copy of the image applied to the top sheet.

Constructions containing a first substrate surface, on which is coated the encapsulated color-former, and a second substrate surface, on which is coated a developer, are often prepared. The coated first substrate surface is positioned within the construction in contact with the coated second substrate surface. Such a construction is known as a "set" or a "form-set" construction.

Substrates, with one surface, on which is coated the encapsulated color-former, and a second, opposite surface, on which is coated a developer, can be placed between the CF and CB sheets in a construction involving a plurality of substrates. Such sheets are generally referred to herein as "CFB" sheets (i.e., coated front and back sheets). Of course, each side including color-former thereon should be placed in juxtaposition with a sheet having developer thereon. CFB sheets are also typically used in form-sets. In some applications, multiple CFB sheets have been used in form-sets. These contain several intermediate sheets, each having a developer coating on one side and a coating with capsules of color-former on the opposite side. Thus, the sheets in the form-set are sequenced in the order (from top to bottom) CB, CFB(s), and CF. This insures that in each form-set a color former and a color developer will be brought into contact when the microcapsules containing the color-forming material are ruptured by pressure.

An alternative to the use of CB, CF, and CFB sheet is the self-contained (SC), or autogenous, carbonless paper in which both the color-former and developer are applied to the same side of the sheet and/or are incorporated into the fiber lattice of the paper sheet.

The conventional method of preventing or minimizing the rupture of capsules by the pressure exerted when carbonless copy paper is handled is by addition of spacer particles, to the coating containing the capsules. These spacer particles are usually referred to as stilt particles or simply as "stilt." Stilt particles may be of many different compositions, but have the common property of being inert to the solvents used in the capsules and being from 1.5 to about 2.5 times the size of the capsules.

Cellulose fibers have been used as stilt material, and U.S. Patent No. 4,630,079 describes use of such fibers with a specified fiber length for such use. Cellulose fibers have a tendency to "mat up" on coaters used to coat carbonless papers and thus cause problems during manufacture of carbonless paper sheets. Another stilt material, described in U.S. Patent 3,625,736, uses particles composed of a water insoluble polymer with a size of 1.5 to 2.0 times that of the capsules. EP 0,017,385 describes the use of starch stilt at a level of at least 150% of the capsule weight. Likewise, EP 0,011,367 also describes the use of starch as stilt material.

Dutch Patent 70/05,045 compares the efficiency of different starches as stilt materials for carbonless paper. Tests for imaging in a typewriter (typewriter intensity test) and for handling resistance (friction staining test) determined starch derived from arrowroot to afford the best stilt material.

Johnson, et al., U.S. Patent No. 4,280,781, describes the use of classified wheat starch as stilt materials for carbonless papers. They found the fraction of wheat starch from 12 to 40 microns in size with at least 22% of the particles being 22 microns or larger was equivalent to arrowroot starch in friction staining resistance. Fractionation required a cyclone separator to produce the large sized particles suitable as a stilt material. However, since arrowroot starch is scarce and expensive, wheat starch is a desirable substitute.

In a second patent, U.S. Patent No. 3,996,061, the disclosure of which is incorporated herein by reference, Johnson, et al., teach that starch obtained from refined legumes such as yellow field pea and faba bean is also equivalent to arrowroot starch as stilt material in carbonless paper. They based their comparisons on typewriter intensity and friction staining tests. They report the primary advantage of these starches lies in their relatively lower cost and higher availability. They did not evaluate the carbonless copy paper in high speed electrophotographic machines or in offset printing presses.

Both of the above Johnson patents teach the equivalence of wheat starch, arrowroot starch, and refined legume starches as stilt materials for carbonless papers.

Carbonless paper is often used in the form of printed form-sets for preparing multiple copies of receipts, bills, and other business forms and form-sets are prepared by collating from 2 to 8 sheets. Form-sets are typically made by applying an adhesive to the edge of a stack of the carbonless paper. Each of the coated sheets in a form-set is somewhat porous and permits the adhesive to penetrate into the pores of the paper, such penetration being necessary to attain satisfactory adhesion of sheets within the form-set. Adhesives useful for edge-padding carbonless papers are described, for example, in U.S. Patent No. 5,079,068, the disclosure of which is incorporated herein by reference.

The adhesively bound papers are then "fanned-out" to separate into individual form-sets. To promote separation, carbonless copy paper form-sets often have a release coating (for example, a fluorocarbon or silicone coating) applied to at least one of the outer faces of each form-set. These coatings are often referred to as "pad coats." Pad coats function as an adhesive (or non-adhesive) to provide low adhesion properties to the outer faces of a form-set; act as a release agent for the edge-padding adhesive; and promote "fan-out properties" in edge padding to allow the adhesively edge-padded stack to "fan-out" or "fan-apart" and separate into

individual form-sets upon fanning. Individual form-sets are prepared by stacking the collated carbonless paper, trimming, edge-padding with an edge-padding adhesive, and fanning-out. "Fan-out" is a method of separating a stack or pad of multiple form-sets into individual form-sets.

Often carbonless paper is prepared and packaged in precollated unpadding form-sets. In one version, referred to as a "straight sequence form-set," the sheets are arranged in the order in which they will appear in the finished form. In these form-sets, the coated back sheet (CB) is first in the form-set, the coated front sheet (CF) is last, and the required number of CFB sheets are in between. Alternatively, the paper may be prepared and packaged in precollated form-sets referred to as "reverse sequence form-sets," wherein sheets of various colors and surfaces are arranged opposite to their normal functional order. The coated front sheet (CF) is first in the form-set, the coated back sheet (CB) is last, and the required number of CFB sheets are in between. When sheets are arranged in this manner and are printed in a printer or copier which automatically reverses their sequence, they will end up in the delivery tray in the proper order for subsequent padding and data entry. The type of sequenced form-set used for a particular printing operation is a function of the printing machinery.

Carbonless paper is widely used in the forms industry and carbonless paper forms have been printed in the past by conventional printing techniques such as offset printing, lithography, etc. With the advent of high speed electrophotographic copiers having dependable, high capacity collating systems and enhanced copy quality, there has been a movement to replace offset printing equipment located in print shops and large "quick-print" installations with electrophotographic copiers. For the successful use of carbonless papers in these copiers, compatibility of the carbonless paper with the machine is critical.

For example, the base sheets upon which carbonless paper coatings are applied to form carbonless papers conventionally imaged via offset printing do not have sufficient stiffness or sufficient sensitivity to machine conditions for curl and moisture control to be handled in copier processors and sorters.

The handling and transfer of carbonless paper through a photocopier can lead to inadvertent rupture of capsules. Capsule rupture releases the encapsulation solvents from within the capsules, and results in exposure of the copier components to the solvent. Solvent exposure causes loss of machine performance, damages copier components, and degrades the quality of photocopies formed.

Capsule rupture also leads to development of smudge marks on the CF coated surfaces because of transfer of the color former from the capsules to the developer.

Capsule rupture also changes the imaging character of the carbonless paper, increasing the sensitivity of the paper and increasing the resistance to inadvertent capsule rupture, herein referred to as "scuff." Sensitivity is an indication of the pressure needed to break the capsules and is significant in form-sets wherein 3 or more copies may be desired or heavier basis weight carbonless papers are used. It is desirable for sensitivity to remain low while "scuff" be as high as possible. Other changes in image density and in the speed of formation of the image may also be affected due to the reduced number of unbroken capsules on the CB sheet.

One solution to the problems encountered when carbonless papers are printed upon in high speed copiers was achieved by Kraft and is disclosed in U.S. Patent No. 4,906,605, incorporated herein by reference. Kraft found that the preparation of carbonless papers using high basis weight paper coupled with smaller capsule size and tighter capsule size distribution, along with the elimination of stilt materials comprising large capsules containing cyclohexane, allows the successful use of these carbonless papers within copiers such as the Xerox 9000 series copiers and printers. Another solution to problems encountered when carbonless papers are used in high speed copiers is taught by Kraft in U.S. Patent No. 5,084,433, incorporated herein by reference. In this patent, Kraft discloses the use of improved solvents compatible with electrophotographic copiers.

A major problem encountered when precollated carbonless papers are used in friction fed machines is the formation of dense, noticeable smudge marks on CF sheets. Smudging occurs when two or more carbonless paper sheets enter the feed mechanism together and is believed to be caused by inadvertent capsule rupture and transfer of color-former from CB to CF surface. This problem is particularly acute when the copier uses a pressure roller or belt for pick up and feeding the sheet into the copier. This problem was addressed by Beery in WO 89/04804 who attributed the smudge to mechanical locking between the sheets due to the relatively high coefficient of friction between the sheet surfaces. His solution was to modify the feed rollers in the machine to make them softer, so that the pressure exerted on the capsule coated surface was reduced and less pressure was placed over the areas of the sheet engaged by the feed mechanism. While photocopier modification by changing the configuration and hardness of the feeding system represents one solution, machine modification is often costly and requires cooperation of the machine manufacturer. It would be advantageous to decrease smudge mark formation without machine modification. A more desirable solution would be to modify the paper surface to eliminate smudging in machine operation.

Another method of preventing capsule rupture and copier damage is taught in copending U.S. Patent Application Serial Number 08/019,795, incorporated herein by reference. Capsule rupture is reduced by preparing carbonless copy paper sheets in which the coefficients of friction of the various faces of the paper are kept

within 0.1 units of each other. While this provides a dramatic improvement in reducing the extent of background staining in carbonless paper, smudging is still present. Further improvement is desired.

In none of the above described work was there any attempt to reduce capsule rupture by providing improved methods of capsule protection from pressure exerted during feed and transport of carbonless copy paper sheets through electrophotographic copiers, high speed offset printing presses, or laser printers.

SUMMARY OF THE INVENTION

We have now discovered that carbonless paper containing refined legume starch used as stilt material when printed on offset presses, and electrographic and electrophotographic copiers provides an unexpectedly great improvement in smudge and scuff, when compared to the use of other stilt materials such as wheat starch. The incorporation of refined legume starch reduces press and copier contamination and provides a cleaner printed sheet when printed on offset printing presses, electrographic and electrophotographic copier/duplicators when used to print copies on carbonless papers. Incorporation of refined legume starch particles into carbonless paper coatings promotes uniform feeding of carbonless paper sheets into offset printing presses, photocopiers, and laser printers by reducing misfeeds and multi-sheet feeds.

In one embodiment, the present invention provides a novel process for the transfer of an image to the surface of a sheet of carbonless paper comprising refined legume starch as a stilt material. The inventive process comprises the steps of:

- (a) generating a latent image on the surface of an imaging element;
- (b) developing the latent image with toner; and
- (c) transferring the developed image to the surface of a sheet of carbonless paper comprising refined legume starch granules as a stilt material.

In a preferred embodiment, the carbonless paper comprises a donor (CB) sheet and a receptor (CF) sheet wherein the refined legume starch is pea starch and is contained in the dried coating on the donor sheet in amount of from 2 to 45 wt%, and more preferably, from about 4 to 25 wt%, based upon the total weight of the coating contained on the donor (CB) sheet. Preferably, the refined legume starch granules have an average particle size ranging from about 10 to 50 microns and more preferably, from about 20 to 30 microns.

In another embodiment, the present invention provides carbonless paper with an image on the surface thereof produced by the foregoing disclosed inventive process, the carbonless paper comprising refined legume starch as a stilt material.

In still another embodiment, the present invention provides an improved process for offset printing employing carbonless paper comprising refined legume starch granules as a stilt material.

Other aspects, advantages, and benefits of the present invention are apparent from the detailed description, examples, and claims.

DETAILED DESCRIPTION OF THE INVENTION

We have now discovered that carbonless paper with refined legume starch used as stilt material, preferably in the CB coating, when printed in electrophotographic copiers, in offset printing presses, and laser printers is smudged considerably less than similar carbonless paper using wheat starch stilt material. Incorporation of refined legume starch particles into carbonless paper coatings also promotes uniform feeding of carbonless paper sheets into offset printing presses, photocopiers, and laser printers by reducing misfeeds and multi-sheet feeds.

Refined legume starch particles, as described in U.S. Patent No. 3,996,061, when incorporated into carbonless paper as a stilt material, provide a completely unexpected improvement in the appearance of the printed sheet and reduce press and copier machine contamination compared to that observed when a wheat starch or other stilt materials are used. Carbonless papers printed on offset presses, electrographic or electrophotographic copier/duplicators, and laser printers, display less smudge and scuff and exhibit reduced capsule rupture when compared with papers incorporating other stiling materials such as wheat starch.

While the use of arrowroot starch as a stiling material might prove to be similar in smudge reduction to that of refined legume starch, the practical disadvantages of arrowroot starch (e.g., scarcity and expense) makes its use of only academic value. The art described by Johnson and coworkers, discussed earlier herein, would lead to the conclusion that the printed carbonless copy paper prepared with wheat starch stilt would be equivalent in performance and degree of capsule rupture to that when refined legume starch stilt was used. The great improvement in the appearance of carbonless paper containing refined legume starch printed on offset presses, electrographic and electrophotographic copiers, and laser printers is, therefore, unexpected. Printed sheets of carbonless copy paper containing refined legume starch are relatively free of any smudge

normally generated when the printing operation causes capsule rupture.

Prior to the discovery of the present invention, form-sets of printed carbonless paper used in commerce for credit applications, credit card receipts, applications for employment, and similar purposes suffered from the formation of smudge and background discoloration during the printing operation of the carbonless paper. These smudges were caused by rupture of capsules containing the solution of color-former in the carbonless paper.

This difference was observed not only in the smudge introduced, but also in tests for sheet sensitivity and for scuff.

It is thought that any commercially available form of refined legume starch, such as pea starch manufactured and sold by Woodstone Foods, Ltd, of Winnipeg, Manitoba, Canada under the name of Accugel, may be used in the present invention. Preferably, the refined legume starch granules have an average particle size ranging from about 10 to 50 microns and more preferably from about 20 to 30 microns.

The refined legume starch may be used in any type of carbonless copy paper such as self-contained (SC) constructions, or those which comprise coated donor (CB) and receptor (CF) sheets. When used in constructions comprising CB and CF sheets, the refined legume starch granules are present in the coating on the donor (CB) sheet in an amount of from about 2 to 45 wt%, and more preferably from about 4 to 25 wt%, based upon the total weight of the CB coating.

Carbonless papers having microcapsules coated thereon are subject to premature rupture of capsules when subjected to pressure. Photocopiers and offset presses typically apply pressure to the paper sheets in many stages of machine operation. This results in capsule rupture. Preferentially, the larger capsules are ruptured. Destruction of these capsules and release of color-former cause smudging. Capsule rupture also changes the imaging characteristics of the carbonless paper, decreasing speed of image formation and making the paper less sensitive. Other changes in image properties may also be affected due to the reduced number of unbroken capsules on the CB sheet and increased resistance to further capsule rupture.

The use of electrophotography, also known as xerography, to prepare plain paper copies of an original is well known and involves the use of a light-sensitive material known as a photoconductor. A photoconductor is a material that is an insulator in the dark and which has the property of being able to transport electric charge when exposed to light.

In the process of the present invention, a latent image can be generated on the surface of a suitable imaging element utilizing either an electrographic or an electrophotographic process. An "electrographic process" is one which involves the production of images by addressing an imaging surface, normally a dielectric material, with static electric charges (e.g., as from a stylus) to form a latent image which is then developed with a suitable toner. The term is distinguished from an "electrophotographic process" in which an electrostatic charge latent image is created by addressing a photoconductive surface with light. The photoconductor may be either organic or inorganic.

In the present invention any conventional solid or liquid toner can be used, although solid toners are preferred. Both types of toners are well known in the art and hence, do not require a great deal of elaboration herein. Solid toners typically contain a pigment or colorant, such as carbon black, either dispersed in or coated with a thermoplastic material. Liquid toners typically are in form of organosols comprising a pigment dispersed in a non-conductive, hydrocarbon medium.

The latent image generated on the surface of the imaging element is developed with toner in any conventional manner, such as by electrophoretic or electrostatic disposition of the toner on the surface of the imaging element.

The developed image may then be transferred from the surface of the imaging element to the surface of the carbonless copy paper by any conventional method used in either electrography or electrophotography such as by utilizing heat and/or pressure or the application of an electric field.

As mentioned earlier, the advent of high speed electrophotography and copiers having dependable, high capacity, collating systems, has resulted in attempts to print carbonless paper on these machines. In order for paper to function properly in a photocopier, a balance must be struck between the various properties that affect print quality and paper handling within the machine. These balances were discussed by Green in a paper on "Functional Paper Properties in Xerography" (see C. J. Green, *Tappi*, **1981**, 64(5), 79-81). He noted that print quality and paper handling are related to the smoothness, electrical resistivity, curl (sheet flatness), stiffness, moisture content, porosity, friction, finish, and wax pick of the paper and that very often the requirements for print quality conflict with those for paper handling. For example, smooth papers give better fix (toner adhesion), but rough papers give better feed properties and paper transport.

M. Scharfe in *Electrophotography Principles and Optimization*; Research Studies Press, Ltd.: Letchworth, England, **1984**; pp. 5-9 describes seven basic steps in the xerographic process. These steps include: charging the photoconductor, exposing it to light to produce an electrostatic latent image, developing the image, trans-

ferring the image to paper, fusing the toned image to paper, cleaning the photoconductor, and erasing the image.

In some high-speed copier/duplicators this cycle takes place very rapidly and 90 - 135 copies/minute can be produced. This requires the copier/duplicator be in good adjustment and close tolerances be maintained and paper transport must be trouble free.

The use of electrophotography to print onto carbonless papers has met with limited success for a variety of reasons. One major problem encountered with printing onto carbonless papers *via* high speed copiers is capsule rupture. This results in formation of paper lint, paper dust, capsule detritus, and capsule fill each of which may act as a nucleus for toner transfer in background areas or react with machine components.

When carbonless paper is printed in an electrophotographic copier, capsule rupture may occur at several places in the copier where pressure on the paper is used to facilitate movement of the sheet through the copier.

The first place where premature capsule rupture may take place is the feed assembly station where paper is fed into the copier from the paper tray. Here, feed rollers introduce the top sheet from the stack of carbonless paper into the machine's paper path. The feeding of paper into printing presses or electrophotographic copiers depends upon individual sheets being fed from a stack of the paper, and the mode of transfer of the sheet into the printing press or photocopier varies with the machine. Printing presses and electrophotographic copiers are designed to feed paper into the machine by several mechanisms. The paper may be fed by a vacuum pickup and transfer system, by a roller or belt which exerts pressure on the top sheet in the stack, by a roller or belt which exerts pressure on the top sheet in the stack in combination with a retard roller or belt beneath the stack, or by other suitable means. The success in feeding single sheets depends upon cleanly separating each sheet from the sheet underneath without dragging the second sheet or multiple sheets into the printer. In the case of carbonless paper, there are several sheets and the sheets have coatings which differ in surface character. Abrasion and resultant capsule rupture occur due to friction feeding between, for example, feed and retard belts and then as the paper is nipped between steel and polymeric rollers. A common mode of contamination at this location is from the buildup of capsule detritus on the feed assembly rollers which later can flake off and transfer into the copying machine itself. Such flakes manifest themselves as large, irregularly shaped spots on the printed forms which usually appear after about 20,000 copies have been run on the machine.

In one common mechanism, a roller or belt pressed against the top sheet of the paper stack is employed as the feed means. These feed means move into engagement with the top sheet of the stack, exert pressure on the top sheet, usually by buckling the sheet, and releases and separates the sheet from the stack. The sheet can then be fed through "take away rolls" into the copier. The feed means usually remain at a fixed position in relation to the stack during sheet feeding.

In another feed system, a forward moving belt removes the top sheet from a stack of paper and advances the sheet to a set of pinch rolls which then feed the sheet into the imaging and toner transfer stations. To prevent double feeds, a retard roller under the feed belt catches any second sheet that begins to transfer with the top sheet.

When carbonless papers are employed in feed mechanisms containing rollers, belts, or retard mechanisms, a smudge mark often develops on the CF surface of a sheet. Smudging is caused by CB capsule rupture and color-former transfer to the CF surface. Capsule rupture can be caused by the feed mechanism (such as a belt or roller) sliding across the paper. Capsule rupture can also be caused by double or multiple sheet feeds of carbonless papers into the feeder assembly and subsequent abrasion by the retard roller along the CB surface. Transfer of color-former from the CB sheet to the CF surface can take place in the paper feed mechanism as another sheet is fed, within the copier, or in the collection tray as the sheets lie on top of each other.

A second location for capsule rupture is at the toner transfer station. The paper travels between the photoreceptor and a bias transfer roll where it is subjected to shear and pressure forces. Capsule rupture at this site causes release of the encapsulated solution of the color-former. The released solvent can wet the surface of the bias transfer roll and come into contact with toner. Toners are typically made of pigments such as carbon black in a polymer such as styrene-butyl methacrylate copolymer and can be readily plasticized by the color-former solvent to a soft tacky state. Transfer of these plasticized toner particles from the bias transfer roll back to the photoreceptor, referred to as "photoreceptor spotting," results in spots on the photoconductor and causes spots on the photocopies after a number of sheets have been printed. Alternatively, the plasticized toner can retransfer from the photoreceptor to the paper in non light-struck (i.e., background) areas to form specks about 200 to 300 microns in diameter. Thus, it is very important to have the copying machine in proper adjustment at this location to minimize such forces which are obviously detrimental to capsule integrity.

A third location where pressure is applied to the paper during the photocopying process is at the heat/pressure toner fusing station. Here, the surface temperature of the heat roller is about 204°C (400°F) and the pressure is thought to be about 140 psi. Pressure at these points can again cause capsule rupture and release of the encapsulated color-former solution with resultant reduced performance of the carbonless sys-

tem.

Throughout the machine, capsule rupture and release of encapsulation solvents can result in exposure of the copier components to the solvent and solvent vapors. Copier components particularly sensitive to solvent are wires which serve the purpose of transferring electrical charges to photoconductor belts, copy paper, or toner. Solvents may react with ions generated by these wires to form compounds that interfere with the function of these wires and other machine components and cause poor machine performance. The wires may be single wires or units commonly referred to as a corotron or a dicorotron. These wires are described in U.S. Patent No. 4,086,650.

When carbonless paper is printed on an offset press, capsule rupture may occur at several places in the press where pressure on the paper is used to facilitate movement of the sheet during printing. For example, in a table feed offset press, drive rollers buckle a sheet paper and feed it to a grip mechanism. Pressure exerted by the drive rollers can break capsules. The grip mechanism grabs the edge of the paper and feeds it into the printing mechanism. The pressure exerted by the grip mechanism can also break capsules. In the printing region, the paper is fed between a blanket roll and an opposing impression cylinder. In this region, where machine adjustment is critical to insure efficient and uniform ink transfer to the paper under controlled pressure, additional capsule rupture can occur.

The present invention will be further described by reference to the following detailed examples. These examples are presented to illustrate the advantages and operation of the invention and are not to be construed as limiting its scope.

EXPERIMENTAL EXAMPLES

Imaging Evaluation of Coated CB Sheets

Carbonless papers prepared with various stilt materials were evaluated before and after being printed in various electrophotographic copiers, and on offset printing presses. The printed papers were evaluated to determine changes in sensitivity, scuff, smudge, image speed, and ultimate image density. In addition to these tests, the amount of smudge originating in the copying or printing operation was measured. Tests were performed on coated CB sheets to determine their characteristics and acceptability for use. These tests include evaluation of imaging speed, and ultimate image density. Imaging speed measures the time to achieve an image acceptable for viewing and is controlled by the kinetics of the imaging reaction, while ultimate image density measures the image after complete reaction and is a measure of the thermodynamics of the imaging reaction.

Imaging speed was determined by passing a CB and a CF sheet under a steel roller with an impact pressure of approximately 350 pli (pounds per linear inch) and measuring the reflectance of the resultant image four seconds after imaging. A Photovolt Model 670 Reflectance Meter with a Model 610 Search Unit fitted with a green filter was used. This instrument is available from Seragen Diagnostics, Inc., Indianapolis, IN. In interpreting reflectance numbers, a high number indicates high reflectance, and a low number indicates low reflectance. Thus a white surface would have a reflectance of close to 100, and a black surface would have a reflectance approaching zero. A "slower" imaging system would be expected to have a greater reflectance after 4 seconds than a faster imaging system. A high speed number indicates a weak, light image. A low speed number indicates a strong, dark image. Thus, the lower the value for speed, the darker the 4-second image. Lower speed values are desired.

Ultimate image reflectance was also measured using the Photovolt Model 670 Reflectance Meter. Following image formation the imaged sheet was heated to $215 \pm 5^\circ\text{F}$ ($102 \pm 3^\circ\text{C}$) for 7 seconds to fully develop the image, and the reflectance was measured. A high ultimate image number indicates a weak, light image. A low ultimate image number indicates a strong, dark image. Thus, the lower the value for ultimate image, the darker the image. Lower ultimate image values are desired.

Sensitivity was determined by placing a strip of CB paper on a strip of CF paper so as to form a 2-part form-set and then scribing the form-set with a set of ball point pens set $15/32''$ apart with sufficient pressure to form a good image on the front surface. The form-set was then heated to $215 \pm 5^\circ\text{F}$ ($102 \pm 3^\circ\text{C}$) for about 10 seconds to fully develop the image. The optical density of the image was measured with a Photovolt Reflection Meter Model 670. A high sensitivity value indicates a weak, light image. The lower the sensitivity value, the more apparent the image is to a lighter pressure. Lower sensitivity values are desired.

Scuff was determined by placing a strip of CB paper on a strip of CF paper so as to form a 2-part form-set and then applying a weight such that the two surfaces were in intimate contact but no capsules were broken. The CF sheet was then pulled across the CB sheet to initiate capsule rupture by the abrasive action of the movement of one sheet on the other. The CF sheet was then heated to $215 \pm 5^\circ\text{F}$ for about 10 seconds to fully

develop the image. The image density was again measured with a Photovolt Reflection Meter, Model 670. A high scuff value indicates a weak, light image. A low scuff value indicates a strong, dark image. Thus, the higher the scuff value, the more resistant the carbonless paper is to scuff. Higher scuff values are desired.

Smudge is defined as the percent reflectance of the mark created in printing in the press or copier. The intensity of the smudge introduced at the leading edge of the paper by the pressure feed rolls was determined by measuring the percent reflectance of the smudge and subtracting this number from the base sheet background percent reflectance. Smudging results from CB capsule rupture during paper feed and subsequent color-former transfer to a CF developer sheet. Capsule rupture and consequent smudging is caused by the feed mechanism (such as a belt or roller) sliding across the paper and dragging the CF sheet over the CB sheet or *vice versa*. This commonly takes place under the force of the retard roller and nip rollers of the feed mechanism. The intensity of the smudge introduced at the leading edge of the paper by the pressure feed rolls was then determined by measuring the percent reflectance of the smudge and subtracting this value from the percent reflectance of the base sheet. Thus, smudge indicates the change (i.e. Δ) in percent reflectance. A high smudge value indicates a strong, dark mark. A low smudge value indicates a weak, light mark. It is preferred to have low smudge values.

Manifolding is the number of sheets through which a legible image is reproduced. Manifolding is determined by, for example, the ease of capsule breakage, paper thickness, and sensitivity.

In the examples described below, the color-formers, encapsulation procedures, binders, and coating methods are similar to those described in U.S. Patent Nos. 3,516,846 and 5,084,433, both incorporated herein by reference. As used herein the term "binder" refers to the soluble-starch/styrene-butadiene latex/zinc rosinate in which the capsules and stilt are slurried. The soluble-starch should not be confused with the starch particles evaluated as stilt materials.

Example 1

The following example demonstrates the effect of stilt in reducing smudge introduced by an electrophotographic copier.

A series of three CB formulations was prepared with the following parts by weight:

Material	A	B	C
Water	285 lb	285 lb	285 lb
Capsules (30%)	361 lb	361 lb	361 lb
Stilt	5.4 lb	16.2 lb	32.4 lb
Binders (25%)	220 lb	220 lb	220 lb

The above formulations correspond to 5%, 15%, and 30% stilt based on dry capsule weight. The above formulations were coated to give a coat weight of 1.3 pounds per ream (1300 square feet) on 20 pound basis weight xerographic grade bond paper. The papers were fed through the feed mechanism of a Xerox 1090 copier as a precollated 2 part form-set. These papers were not printed upon in the machine. The intensity of the smudge introduced at the leading edge of the paper by the pressure feed rolls was then determined by measuring the percent reflectance of the smudge and subtracting this value from the percent reflectance of the base sheet. The difference in the amount of smudge generated was very evident upon visual examination of the printed sheets. The lower smudge values and higher scuff values indicate that carbonless papers containing pea starch have a greater tolerance to handling. Scuff values for the coated sheets was also measured. The results are shown in Table 1.

Table 1

- Effect of Stilt on Smudge Generated in Electrophotography				
	Smudge		Scuff	
% Stilt Added	Wheat Starch	Pea Starch	Wheat Starch	Pea Starch
0% stilt	33	33	---	---
5% stilt	31	26	73.0	73.2
15% stilt	27	19	75.2	76.5
30% stilt	20	11	76.1	77.0
	Speed		Ultimate	
% Stilt Added	Wheat Starch	Pea Starch	Wheat Starch	Pea Starch
5% stilt	33.7	33.1	21.6	21.4
30% stilt	35.0	34.5	23.4	22.6

The sheets were then evaluated for speed and ultimate image. The results, also shown above in Table 1, indicate that the two materials behave in a similar manner before being printed upon in a copier. Thus these two standard tests for evaluating carbonless paper speed and ultimate image would appear to lead to the conclusion that the two materials are equivalent.

Example 2

Comparison of the properties of the above coated CB sheets incorporating pea starch and wheat starch stilt materials was also made before and after the sheets were imaged and printed upon in various Xerox copiers. The change in properties is an indication of how extensive was the rupture of the capsules during the electrophotographic printing operation. The results are shown in Table 2.

In all cases the changes in sensitivity, speed, and ultimate image were less with pea starch stilt than with wheat starch stilt, indicating less capsule damage when the sheets were imaged in the copier.

When considering the initial differences only between wheat and pea starch, this data might be judged to be very similar and thus the real improvement in after printing results might be missed by someone running only the standard tests for carbonless paper prior to printing such as those performed and reported in Dutch Patent 70/05,045 and in U.S. Patent Nos. 4,280,781 and 3,996,061.

Table 2

- Effect of 30% Stilt in Sheets Imaged in Xerox Copiers					
Model #	Property	Material	Initial	Final	Change (Δ)
Xerox 5090	sensitivity	Wheat Starch	57.8	63.3	5.5
		Pea Starch	59.9	63.7	3.8
	speed	Wheat Starch	38.1	43.9	5.3
		Pea Starch	38.5	42.0	3.5
	ultimate	Wheat Starch	22.7	24.1	1.4
		Pea Starch	22.6	23.1	0.5
Xerox 1090	sensitivity	Wheat Starch	57.8	61.9	4.1
		Pea Starch	59.9	60.4	0.5
	speed	Wheat Starch	38.1	39.9	1.8
		Pea Starch	38.5	39.0	0.5
	ultimate	Wheat Starch	22.7	23.8	1.1
		Pea Starch	22.6	22.8	0.2
Xerox 9900	sensitivity	Wheat Starch	57.8	63.4	5.6
		Pea Starch	59.9	64.0	4.1
	speed	Wheat Starch	38.1	43.8	5.3
		Pea Starch	38.5	43.2	4.7
	ultimate	Wheat Starch	22.7	24.7	2.0
		Pea Starch	22.6	23.6	1.2

Example 3

The following example compares the effects of incorporating different stilt materials on offset press damage of carbonless paper.

A series of formulations was prepared varying the amount of binders and stilts. The stilt materials evaluated were Keestar-328, a wheat starch available from Ogilvie Mills, and Accugel, a refined pea starch available from Woodstone Co., Winnipeg, Canada. The levels of stilt were 0%, 40%, and 70% of the dry capsule weight. In the above tests, the color-formers, encapsulation procedures, binders, and coating methods are again similar to those described in U.S. Patent Nos. 3,516,846 and 5,084,433. All weights are in lb. The capsules accounted for 30.5% of the weight of capsule slurry. The formulations were roll coated to give the coating weights shown in the fifth column. Coat weight is in lb/ream (1300 ft²).

EP 0 620 121 A2

Sample	Weight of Capsule Slurry	Wheat Stilt	Pea Stilt	Coat Weight	Binder Weight
A	479 lb	0 lb	0 lb	1.20 lb	317 lb
B	479 lb	0 lb	0 lb	1.59 lb	317 lb
C	467 lb	58 lb	0 lb	1.41 lb	348 lb
D	467 lb	58 lb	0 lb	1.89 lb	348 lb
E	409 lb	89 lb	0 lb	1.54 lb	333 lb
F	409 lb	89 lb	0 lb	2.03 lb	333 lb
G	478 lb	0 lb	58 lb	1.50 lb	348 lb
H	478 lb	0 lb	58 lb	1.83 lb	348 lb
I	431 lb	0 lb	89 lb	1.54 lb	342 lb
J	431 lb	0 lb	89 lb	2.11 lb	342 lb

These coated sheets were then printed on an offset printing press. The printed sheets and the unprinted sheets were evaluated for scuff, sensitivity, image speed and ultimate image. Results of these tests are shown in Table 3. In Table 3, initial indicates the value before printing in an offset press and final indicates the value after the sheet had been printed on an offset printing press. The column labeled "Change (Δ)" indicates the change in values for sensitivity and scuff between the unprinted sheet and the printed sheet.

Table 3

- Effect of Press Damage on Carbonless Paper Containing Stilt						
	Speed			Ultimate		
Sample	Initial	Final	Change (Δ)	Initial	Final	Change (Δ)
A	35.1	37.5	2.4	21.9	22.6	0.7
B	33.4	33.9	0.5	20.3	20.3	0.0
C	37.2	38.9	1.7	22.8	22.9	0.1
D	34.6	35.2	0.6	20.7	20.9	0.2
E	36.9	37.0	0.1	23.3	23.5	0.2
F	35.7	35.0	-0.7	21.4	22.0	0.6
G	33.7	34.3	0.6	20.5	21.6	0.1
H	34.7	31.7	-3.0	19.3	19.3	0.0
I	35.9	36.6	0.7	20.9	21.1	0.2
J	35.3	33.0	-2.3	20.2	20.1	-0.1
	Sensitivity			Scuff		
Sample	Initial		Change (Δ)	Initial		Change (Δ)
A	57.5		6.9	71.6		5.8
B	59.8		5.0	73.8		3.0
C	62.3		4.1	76.9		2.1
D	66.6		3.0	78.4		0.9
E	68.4		2.1	80.0		0.2
F	72.7		-0.4	79.8		-0.6
G	63.1		2.8	78.6		0.2
H	66.9		1.1	79.2		0.7
I	66.9		0.8	78.5		1.2
J	72.6		-0.3	79.3		0.2

The change (Δ) between the initial and final values in Table 3 is an indication of how extensive the capsule rupture is in the printing operation. In sample A where no stilt is present, and the coat weight is 1.2 pounds/ream the sensitivity increases 6.9 units, indicating large amounts of capsules were destroyed in the printing step. Scuff also increased by a large amount, 5.8 units, which also indicates extensive capsule rupture. In sample C where wheat starch stilt was used at a 40% level (based upon dry capsule weight) and the coat weight of capsules was about the same as A, the sensitivity increased by 4.1 units and the scuff value increased by 2.1 units. This indicates less capsule rupture during printing and that the wheat starch is indeed affording increased capsule protection. In sample G, a comparable set of data for paper made with pea starch at the 40% level showed an increase in sensitivity of only 2.8 units (much less than the 4.1 units observed for the wheat starch). Similarly, the increase in scuff for the coating containing pea starch as stilt was only 0.2 units. This is a major reduction in capsule rupture over that seen without stilt (5.8 units) and over that seen with wheat starch (2.1

units).

At higher coat weights with 40% stilt material, a comparison of Samples D and H indicates the same trend is apparent. Sensitivity for carbonless paper containing pea starch paper increased 1.1 units while sensitivity for carbonless paper containing wheat starch increased by 3.0 units. Similarly, scuff increased 0.7 units for carbonless paper containing pea starch and 0.9 units for carbonless paper containing wheat starch.

Similar comparisons between Samples E and I; and F and J confirm the superiority of carbonless papers incorporating pea starch as stilt materials over carbonless papers incorporating wheat starch as stilt materials.

As noted in Example 1, a comparison of the change in image speed and ultimate image does not indicate any advantage for one stilt over the other. Statistical analysis showed both stilts affected the initial sensitivity equivalently, while legume starch increased initial scuff values significantly.

Example 4

The following example demonstrates the effect of the type of stilt on smudge and scuff after printing in an electrophotographic copier.

CB sheets, prepared as in Example 2, were imaged in a Xerox 1090 copier and evaluated for smudge and scuff. The results, shown in Table 4, demonstrate that at both high and low coating weights, pea starch provides both lower smudge and higher scuff values than wheat starch. The lower smudge values and higher scuff values indicate that carbonless papers containing pea starch have a greater tolerance to handling.

Table 4

- Effect of Stilt Type on Sheets imaged in a Xerox 1090 Copier				
% Stilt	Stilt Type	Smudge	Scuff	Coating Weight
0%	None	20.7	72.7	1.2
40%	Wheat Starch	17.1	75.3	1.41
40%	Pea Starch	12.3	77.1	1.50
70%	Wheat Starch	13.8	77.3	1.54
70%	Pea Starch	8.4	78.6	1.54
0%	None	27.3	70.5	1.59
40%	Wheat Starch	12.0	76.6	1.89
40%	Pea Starch	7.7	77.9	1.83
70%	Wheat Starch	8.3	78.3	2.03
70%	Pea Starch	6.1	79.0	2.11

Example 5

The following example compares the effect of different loadings of wheat starch and pea starch stilt materials on the sensitivity of sheets before and after imaging. CB sheets, coated as in Example 2, were prepared and imaged in a Xerox 9900 copier. The sensitivity of the sheets was determined before (initial) and after (final) imaging in the photocopier and the change (Δ) in sensitivity determined by subtraction. The increase in sensitivity values of carbonless papers incorporating pea starch as a stiling material is much lower than samples incorporating wheat starch as a stiling material. This indicates much less capsule rupture during the printing operation.

Table 5

- Effect of Stilt on Sensitivity of Sheets Imaged in a Xerox 9900 Copier					
% Stilt	Stilt Material	Coating Weight	Sensitivity		
			Initial	Final	Change (Δ)
0%	None	low	56.1	62.2	6.2
40%	Wheat	low	61.1	66.4	5.3
40%	Pea	low	63.2	65.2	2.0
0%	None	high	58.1	62.3	4.2
40%	Wheat	high	65.0	68.0	3.0
40%	Pea	high	66.7	66.2	-0.5

Example 6

The following Example demonstrates the effect of using various binders with stilts materials on smudge. A formulation was prepared with a binder of Vinol 205 polyvinyl alcohol (13 wt. % solids, available from Air Products Co., Allentown, PA) in place of the latex/starch combination of the prior examples. The capsule/binder ratio in this formulation was more than double that in the earlier examples. The formulation was prepared by mixing:

Water	416 lb
Capsules (wet)	454 lb (177 lb dry wt)
Stilt	55 lbs
Binder Materials (11.4%)	275 lb

The stilt used was again wheat starch or pea starch. A control formulation was prepared without stilt, as well. The formulations were coated to give a coat weight of 1.2 pounds per ream. The sheets were printed in a Xerox 1090 photocopier and the smudge and scuff were measured, with the following results.

Table 6

- Effect of Stilt With Poly(vinyl alcohol) Binders on Xerox 1090 Copier Stain			
Sample	Smudge	Scuff	Coating Weight
Control (No Starch)	45.8	60.6	1.18
	35.2	63.9	1.53
40% Wheat Starch	23.6	73.6	1.32
	23.0	72.5	1.60
40% Pea Starch	20.1	74.2	1.08
	16.6	75.4	1.42

The data again clearly demonstrate the superiority of pea starch stilt over wheat starch stilt in preventing

staining by handling (as shown by the scuff data) or by machine operation (as shown by the smudge data).

The above data were evaluated by regression analysis to obtain coefficients for sensitivity and scuff. The results shown below indicate that addition of stilt at a given level increases both scuff and sensitivity. Since sensitivity is a measure of the amount of pressure needed by the imaging stylus, lower values allow more legible copies to be made when the form-set contains 3 or more copies. Higher scuff values, however, allow more abuse of the paper without the rupture of capsules and the ensuing stain of the copies. The coefficients show the scuff/sensitivity ratio to be superior for pea starch. Both stilt materials increase sensitivity to about the same extent but the pea starch is definitely superior in increasing the scuff and giving better handling properties.

Stilt Material	scuff coefficient	sensitivity coefficient	scuff/sensitivity ratio
Wheat starch stilt	18.60	25.05	0.744
Pea starch stilt	23.82	26.78	0.889

Reasonable variations and modifications are possible from the foregoing disclosure without departing from either the spirit or scope of the present invention as defined in the claims.

Claims

1. A process for the transfer of an image comprising the steps of:
 - a) generating a latent image on the surface of an imaging element;
 - b) developing said latent image with toner; and
 - c) transferring said developed image to the surface of a sheet of carbonless paper, said carbonless paper comprising refined legume starch granules as a stilt material.
2. The process according to Claim 1 wherein said refined legume starch granules have an average particle size in the range of from about 10 to 50 microns.
3. The process according to Claim 2 wherein said refined legume starch granules have an average particle size in the range of about 20 to 30 microns.
4. The process according to Claim 1 wherein said refined legume starch granules are refined pea starch granules.
5. The process according to anyone of Claims 1 to 4 wherein said carbonless paper comprises a donor sheet and a receptor sheet.
6. Carbonless paper with an image on the surface thereof produced by the process of anyone of Claims 1 to 5.
7. In an offset printing process wherein an image is transferred onto the surface of a sheet of carbonless paper, the improvement which comprises employing carbonless paper comprising refined legume starch granules as a stilt material.
8. The process according to Claim 7 wherein said refined legume starch granules are refined pea starch granules.