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(54) Removable nonporous opaque thin film layer

(57) A composite imaging sheet for use in copying and printing machines comprising a transparent imageable sheet having a machine direction and a transverse direction, and two major surfaces, each surface having four edges having edge portions coextensive therewith, the sheet bearing a releasable thin opaque film layer having a total thickness of from 5 µm to 60 µm and a film thickness of no greater than 30 µm, on at least one edge portion of one surface of said imageable sheet, the thin film layer having an opacity of at least 70%, and a tensile energy to break of at least 0.1 joule.

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Description

Background of the Invention

Field of the Invention

The present invention relates to transparent imaging sheets for use in printers and copiers. More specifically, the present invention relates to a composite sheet having a releasable non porous opaque thin film layer attached to an edge portion of the transparent imageable sheet.

Description of the Art

Copiers and printers usually employ sophisticated mechanisms to allow them to select a single imaging sheet from a stack of such sheets and, by means of rollers, wheels, belts, and the like, cause each such sheet to be rapidly and precisely moved past various points in the machine which image and process the sheet. In this way, large numbers of copies can be made in a short time. Further, the automated feeding means that an operator need not tend the copier during such process. A large number of sheets is stacked in the feeding tray of the copier or printer, and combinations of optical sensing mechanisms (which may be transmissive or reflective), and mechanical methods are used to detect the passage of sheets. These sensing mechanisms will halt the operation if jamming occurs to avoid any damage to the machine.

Transparent films, by their nature, cannot be detected by optical sensors. In order for such sensing mechanisms to operate, the sheets need to be at least partially opaque to interrupt the light beams employed in the photosensing mechanisms. Otherwise, transparent sheets will not operate in such machines.

In order to render transparent sheets useful in these machines, two different solutions have been used to form an opaque area readable by the sensor. Most commonly, a paper backing has been used; however, synthetic paper and some thicker films have been disclosed. The paper or other opaque body is typically releasably adhered to the transparent imaging sheet by means of a thin line of adhesive. The paper may cover only a portion of the sheet, e.g., it may be a stripe along the leading edge portion of a plane opposite to the image transfer plane of the transparent film such as that disclosed in Sho 58-187743, or for machines requiring larger opaque areas, a full sheet of paper substantially coextensive with the imaging sheet, such as described in CA 1184951. When the transparent sheet has been imaged, the operator removes the paper from the transparent sheet and discards the paper.

Paper backings and thick film backings work quite well for opacity, and may be designed to be easily releasable from the imaging sheets after imaging; however, the backings disclosed insulate the sheets from contact with the heated fuser which can result in insufficient fusing in copier machines. Further, the paper used for such stripes is usually quite thick and therefore the edge portion bearing the paper backing is much thicker than the portion of the sheet not bearing the paper backing. When a large number of sheets are put into the feeding tray, the thickness of the combination of paper stripes at one edge of the sheet causes one side of the stack to be almost twice as tall as the other side. This results in feeding problems, as well as substantially limiting the number of sheets which can be stacked at one time. Another problem occurs in imaging machines which pick up a sheet in the center of the sheet stack. In these machines, the sensor for the stack will give a false reading and the mechanical means will not lower to the correct height to select a sheet.

Color copiers have two problems with transparent imaging sheets. First, most color copiers require that such sheets be bypass fed rather than tray fed. In some models, this means single sheet bypass feeding by an operator. The bypass feeding causes a slower trip through the fuser, increasing the fuser contact time, thus ensuring complete fusing of the transparent imaging sheet. Second, tray feeding, possible only if the imaging sheet can simulate a sheet of paper to the sensor, causes a faster trip through the fuser, which reduces the fuser contact time. This makes the fusing much more heat transfer limited, and may result in incomplete fusing of the color image. If the imaging sheet has a backing or stripe, the insulative property thereof reduces fusing even further, typically resulting in visible degradation of color image quality.

The other alternative, useful where only a small portion of the transparent sheet need be opaque is the printing of a dark line along the top or side of such sheet such as that disclosed in Sho 56-204005.

U.S. Patent No. 5,126,762 discloses a recording sheet having a mark for permitting the determination of sheet feeding as well as differentiating between front and back surfaces of the sheet. The sheet comprises an optical functional portion disposed along at least one edge of the sheet and arranged asymmetrically with respect to the center of the edge and having a functional feature regarding light different from that of an image forming portion of the sheet.

These composite sheets can be stacked into a tray without causing feeding problems as the thinness of the printed line or lines does not cause stacking problems. However, such thin printed lines are not removable after imaging and are visible when projected during a presentation which is not aesthetically pleasing.

Imaging sheets constructed to have an attached overlay, at least a portion of which is an opaque sensing strip, are disclosed in U.S. Patent No. 5,208,093. Such an article preferably comprises a second opaque region, or a tab, underlying the transparent sheet and spaced away from the first opaque strip leaving a transparent window to signal the fuser that a transparency has been fed, so that the fusing speed can be reduced for better fusing. However, this reference prefers porous materials to be used as opaque strips and tabs, and such porous materials are known to be good insulators. Also, porous materials must be relatively thick to have sufficient tensile strength required for clean removal without tearing.

It would therefore be desirable to create a composite imaging sheet having a thin easily-releasable layer, which can be applied in differing positions and sizes during, or immediately after manufacture of the imaging sheet. Such a sheet would provide good automated stacking and feeding in state of the art machines.

It would further be desirable for such thin layer not to having such large insulating effects on the film during fusing, as such insulation reduces the effectiveness of the fusing. Effective fusing is especially important for good image quality in the case of color copiers, but may impact toner adhesion and image quality in black and white copiers as well.

Finally, it would be highly desirable to have a film which would tray feed effectively in a color copier, especially in those copiers which only allow single sheet bypass feeding of transparency films.

It has now been discovered that the use of a nonporous opaque thin film layer provides improved multiple sheet feeding, while minimizing the insulative characteristics. These sheets therefore, exhibit more complete fusing, and attendant improved image quality and have sufficient opacity to be tray fed.

Summary of the Invention

The present invention provides a composite imaging sheet for use in copying and printing devices which has a nonporous opaque thin film layer which allows a transparent imaging sheet to be used in machines having optical sensors. The nonporous opaque thin film layer provides such benefit without insulating the sheets, which allows full fusing in copier machines. The composite sheet stacks easily in such machines and large numbers may be fed both from side selecting and midpoint selecting machinery. The nonporous opaque thin film is easily removable after imaging so that the final imaged transparency has no distracting dark line or area when projected during a presentation.

Specifically, the composite imaging sheet of the invention comprises a transparent imageable sheet having a machine direction and a transverse direction, said sheet having two major surfaces, each surface having four edges with edge portions coextensive therewith, said sheet bearing a releasable nonporous opaque thin film layer having a total thickness of from 5 to 60 µm and a film thickness of no greater than 30 µm on at least one edge portion of one surface of said imageable sheet said thin film layer having an opacity of at least 70%, and a tensile energy to break of at least 0.1 joule, said film layer being cleanly released from said imageable sheet.

Preferred composite imaging sheets of the invention comprise a nonporous opaque thin film layer having an opacity of at least 75% and a tensile energy to break of at least 0.25 joule, said nonporous opaque thin film layer being cleanly releasable from said imageable sheet.

For those composite sheets of the invention specifically designed for use with color copiers, the projected color image of an imaging sheet of the invention will exhibit an increased pastel haze (Δ Pastel Haze) of no more than 10% when measured in regions of the image overlaid by the nonporous opaque thin film layer. This value is based on a reference sheet having no attached nonporous opaque thin film layer.

In an especially preferred embodiment of the invention for color copiers, the nonporous opaque thin film layer has a machine direction width which is sufficient in size to simulate paper to the sensor. It is believed that this is the first time tray feeding of transparency films has been possible on most color copiers.

Once formed, the nonporous opaque thin film layer remains attached to the imaging sheet throughout the printing and copying process until manually removed.

The opaque thin releasable opaque film layer can vary in total thickness from 5 µm to 60 µm, preferably from 5 to 35 µm. The film thickness varies, but must be no greater than 30 µm, preferably 25 µm or less. The thinness of this layer makes it possible to allow from 3 to 10 times as many of these composite sheets to be stacked into the feeding tray of a printer or copier as conventional sheets without significant insulating effect or feeding problems. Because the opaque edge portion of the composite imaging sheet does not insulate the imaging sheet, incomplete fusing problems, and resultant degradation of images are not encountered. This is even true for images made at tray-feed speeds in color copiers.

The releasable nonporous thin opaque film layer has adhesive characteristics, i.e., either the layer is directly coated on or it is attached by means of an adhesive composition. Whichever method is used, the layer can be cleanly removed from the transparent sheet even after imaging. Surprisingly, the thin layer possesses sufficient tensile strength that the layer is cleanly removable, i.e., no tearing of the layer occurs during removal.

In another embodiment of the invention, the nonporous opaque thin film layer is arranged along multiple, typically two, edge portions of the imaging sheet, such edge portions can either be in a parallel or perpendicular relationship to each other. This allows imaging in either the portrait or landscape positions.

In yet another embodiment of the invention, the nonporous opaque thin film layer can have varying degrees of opacity along the transverse direction of the imaging sheet so that machines having asymmetrically placed sensors will be able to distinguish the imaging surface of the imaging sheet from the opposing surface, and thus prevent jams caused by inverted sheets.

The following terms have the defined meanings when used herein.

1. The terms "film" and "thin film" mean a continuous nonporous polymeric sheet having a film thickness of no greater than 30 µm which is substantially non fiber containing.
2. The term "thickness" refers to the dimension measured from the substrate through the coating to the surface, also called "coating height" or "coating depth".
3. The terms "opaque" and "opacity" as used herein mean non-transparent, i.e., the thin film layer has optical properties which cause light blocking, light reflecting or light scattering or a combination thereof to such an extent as to prevent transmission of the majority of light. A majority of light is not transmitted through the edge portion(s) of the transparency bearing the thin film layer thereon.

    The opacity must also be such that the layer is capable of interrupting the light beams employed in the photosensing mechanisms, i.e., it must be at least 70%.
4. The term "total thickness" when used for the nonporous opaque thin film layer means the thickness of the film layer combined with the thickness of the adhesive used to attach the layer, if any, and the thickness of the opaque paint or dye used to render the film layer opaque, if any.
5. The term "film thickness" when used for the nonporous opaque thin film layer means the thickness of the film only, i.e., the actual dried coating height of the film.
6. The term "edge portion" means a portion smaller than the entire imageable sheet, said portion being coextensive with one edge of a major surface. Each major surface has four edge portions.
7. The term "leading edge" means that edge of the paper which is the first edge of the sheet to feed into the copier or printer. Depending on whether a landscape or portrait oriented image is desired, the leading edge may be either length edge of a rectangular imaging sheet.
8. The term "stripe" refers to a nonporous opaque thin film layer having a small machine direction width and therefore having a line or stripe appearance.
9. The terms "striped" and "striped film" mean a film having an opaque layer thereon, either a layer within the scope of invention or a paper layer outside the scope of the invention, as specified.
10. The term "width" means the amount of space that the thin film layer overlays proceeding from the edge of the transparency toward the interior.

All percents, ratios and parts herein are by weight unless otherwise specified.

Detailed Description of the Invention

This invention describes the use of a nonporous opaque thin film layer as a sensing layer or stripe for transparent imaging sheets. Films useful as nonporous opaque thin film layers must have four characteristics; they must be strong enough to be cleanly removable, they must be opaque enough to reliably trip the optical sensor used in copiers, they must have low enough insulative effects to allow complete fusing in order to provide excellent image quality, and they must be thin enough not to cause a large variation in the stack height from the edge portion having the overlaid film layer to the edge portion which does not have a film layer. The top sheet "slopes" down from one edge portion to the other.

Useful films have a tensile energy to break of at least 0.1 joule, preferably at least 0.25 joule. Films or other materials having lower tensile strength than 0.1 joule will have insufficient strength to be cleanly removable, i.e., they will frequently tear when removal is attempted.

This thin layer can be selected from a variety of heat-resistant materials, as long as such materials are available in the requisite thickness, i.e., less than 30 µm, and possess sufficient structural integrity such that no tearing of the layer occurs during imaging or removal. Heat-resistance means that useful films must retain sufficient cohesive strength to be easily removed in one piece from the imaging sheet when normally fused, and when a misfeed results in extended contact with hot fusing rolls. Useful films must have sufficient cohesive strength to allow a clean removal in most samples from the fusing roll should a premature release from the imaging sheet causes retention in the copier machine.

The nonporous opaque thin film layer can be formed from heat-resistant polymer films including, but not limited to, polyolefins such as polyethylene and polybutylene; polystyrene; polyesters such as polyethylene terephthalate (PET); polymethylmethacrylate; cellulose acetate; polyvinylchloride and polyvinylidene fluoride; polyamides and polyimides; and mixtures thereof. Polyethylene and PET are preferred, with PET being highly preferred.

Porous materials, such as those disclosed in U.S. Patent 5,208,093, are not useful as thin film layers of the invention. When such layers are used in typical thicknesses, the stack height variation is on the order of 2; that is, the edge portion of the imaging sheet overlaid by the porous material is close to twice the height of the edge portion having no porous material overlaid. The thick material also has a very large insulative effect. If the porous material is formed into thinner layers, the tensile strength and the opacity decrease drastically while the insulative effect decreases more slowly. This means that layers which are thin enough for the imaging sheets to pass the stack height variation test fail two or even all three other requirements; they typically have opacity values of less than 70%, they have extremely low tensile strength, and may still have insulative values high enough to prevent complete fusing. This is seen by reduced image quality.

When an adhesive is employed for attaching the thin film layer to the imaging sheet, its adhesive properties need to be carefully balanced. The thin film opaque layer needs to adhere firmly to the imaging sheet so that the composite sheet will not be separated during routine handling and packaging, or during imaging in the copier or printer. However, the adhesive must also allow the thin film opaque layer to be readily removed from the imaging sheet without leaving adhesive residues. This must also be true of the adhesive properties of directly coated thin film opaque layers.

Useful adhesives include inherently-tacky, elastomeric copolymer microspheres such as disclosed in U.S. Patents 3,691,140 and 4,166,152; removable adhesives such as disclosed in U.S. patents 4,599,265, 4,855,170, and 5,283,092.

Preferably, the adhesive composition comprises:

1) from 50 to 90 parts by weight of at least one lower alkyl acrylate having an alkyl group comprising from 4 to 12 carbon atoms; and
2) from 10 to 50 parts by weight of at least one higher alkylacrylate having an alkyl group comprising from 12 to 26 carbon atoms.

Photocrosslinker may be added if necessary improve the cohesive strength of the adhesive in order to prevent substantial adhesive transfer to the imaging sheet. The photocrosslinker is preferably present from 0.05% to 1% by weight of the adhesive composition.

This preferred adhesive has high cohesive strength, high tack and high peel strength along with good removability. The adhesive further possesses low melt viscosity and can be easily used as a hot melt adhesive thereby allowing it to be used in an continuous processing line forming the composite imaging sheet.

The total thickness of the nonporous opaque thin film layer (film plus adhesive) ranges from 5 µm to 60 µm, preferably from 5 µm to 50 µm. The film thickness is no greater than 30 µm, preferably from 5 µm to 25 µm. The adhesive layer ranges in thickness from 2.5 µm to 30 µm, preferably from 5 µm to 15 µm. At these thicknesses, the films have good tensile strengths, opacity values, and do not cause stack height variation.

The opacity can be accomplished either by casting a pigment filled composition into a film and attaching the film onto the imaging sheet, or by coating or printing a pigment filled composition or ink. The pigment filled composition can be coated onto a substrate and then attached onto the imaging sheet, or coated directly onto the imaging sheet. A transparent nonporous thin film can also be printed with an opaque ink after attachment to the imaging sheet, if desired.

The degree of opacity needed will depend on the detection methods used in the copier or printer. However, the opacity of the stripe should be at least 70%, preferably, greater than 75% for ease and reliability of detection by the optical sensor.

In one embodiment where opacity is introduced by direct printing of a thin film and attachment of the printed film to the imaging sheet, the degree of opacity is varied along the transverse direction of the thin film layer. This permits the copier or printer to distinguish between the imageable and nonimageable surfaces of the imaging sheet while still sensing that a sheet has been fed when fed in the proper orientation. This permits the coating of only one surface of the transparency, if desired, or coating a different coat on the opposing surface, e.g., a feed facilitation coat, without fear of inverted feeding. Preferably, the opacity of the layer should drop to a level beyond which the opacity will no longer be detected by the sensing device at the center of the transverse direction width. However, since certain machines have centered sensing devices, and others have asymmetrically placed sensing devices, this embodiment of the invention may have an opacity gradient specifically designed for a certain model or series of copiers or printers. Since inverted sheets result in machine jams and possibly, deposits of imageable coatings onto portions of the machine, requiring manual removal and possible down time for cleaning, this embodiment allows multiple worry free feeding, as an inverted sheet will simply not be sensed by the machine, and thus will not feed.

If the nonporous opaque thin film layer is coated or painted directly onto the imageable sheet, the composition must be chosen to permit removability without leaving any unwanted residue on the imageable sheet.

Useful compositions for coating directly onto the imaging sheet include such binders as hot-melt binders, and UV-curable binders, including but not limited to water-soluble polymers such as poly(vinyl alcohol), poly(vinyl pyrrolidone), and gelatin; solvent-soluble binders such as poly(bisphenol-A-ester), e.g., those available under the trade name Atlac® from Reichold Chemical; acrylic resins, urethanes, and the like.

These compositions may contain pigments or dyes for coloring purposes, with the pigment to binder ratio being preferably less than one. Lower ratios of binder in the composition tend to produce brittle layers, whereas higher ratios tend to excessively soften the layers.

Preferred pigments include conventional pigments and dyes such as titanium dioxide, carbon black, metallic oxides, metal powders lead chromates, natural and synthetic dyes and pigments used in inks, fabrics and the like.

The surface of the substrate may be treated to better receive or retain the nonporous opaque thin film layer. However, any treatment to improve adhesion of the stripe to the substrate should not interfere with the removability of the stripe.

The transparency film is generally coated with an imaging layer on at least one major surface. The imaging layer can be any toner-receptive or ink-receptive composition imageable in a copier or printer. Compositions suitable for the imaging layer include a variety of known compositions depending on the machine(s) with which the film is intended for use. Useful imaging compositions include thermoplastic resins such as polyester resins, styrene resins, polymethylmethacrylate resins, epoxy resins, polyurethane resins, vinyl chloride resins, and vinyl chloride-vinyl acetate resins.

If the image-receptive sheet is to be used in a plain paper copier, the imaging coating typically comprises from 65 parts to 99.9 parts of a film forming polymer, which can be any polymer, copolymer or polymer blend capable of water-based emulsion coating or aqueous solution coating, using conventional coating techniques. Such polymers can be made from any ethylenically unsaturated monomers and can include acrylates and methacrylates, styrenes, substituted styrenes and vinylidine chlorides.

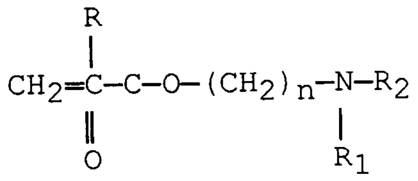
In this embodiment, the film forming polymer contains from 80 parts to 100 parts of at least one monomer selected from the group consisting of bicyclic alkyl (meth)acrylates, aliphatic alkyl (meth)acrylates having from one to twelve carbon atoms, and aromatic (meth)acrylates.

Useful bicyclic (meth)acrylates include, but are not limited to, dicyclopentenyl (meth)acrylate, norbornyl (meth)acrylate, 5-norborene-2-methanol, and isobornyl (meth)acrylate. Preferred bicyclic monomers include dicyclopententyl (meth)acrylate, and isobornyl (meth)acrylate.

Useful aliphatic alkyl (meth)acrylates include, but are not limited to, methyl acrylate, ethyl acrylate, methyl (meth)acrylate, isobutyl (meth)acrylate, isodecyl (meth)acrylate, cyclohexyl (meth)acrylate, and the like. Preferred aliphatic monomers include methyl (meth)acrylate, ethyl (meth)acrylate, and isodecyl (meth)acrylate.

Useful aromatic (meth)acrylates include, but not limited to benzyl(meth)acrylate and styrene (meth)acrylate.

The polymer can also contain from 0 to 20 parts of a polar monomer having the formula:



$$CH_2{=}\overset{R}{\overset{|}{C}}{-}\underset{\underset{O}{\|}}{C}{-}O{-}(CH_2)_n{-}\underset{\underset{R_1}{|}}{N}{-}R_2$$

wherein R is hydrogen or methyl, R_1 and R_2 is selected from the group consisting of hydrogen, identical, and differing alkyl groups having up to 8 carbon atoms, preferably up to 2 carbon atoms; the N-group can also comprise a cationic salt thereof.

Useful examples include N,N-dialkyl monoalkyl amino ethyl (meth)acrylate, and N,N-dialkyl monoalkyl amino methyl (meth)acrylate, N-butyl amino ethyl (meth)acrylate, and the like for emulsion polymers, and quaternary ammonium salts thereof for solution polymers. Preferred monomers include N,N'-diethylaminoethyl(meth)acrylate, and N,N'-dimethylaminoethyl(meth)acrylate for emulsion polymers and bromoethanol salts of N,N'-dimethylaminoethyl (meth)acrylate, and N,N'-diethylaminoethyl(meth)acrylate for solution polymers.

The presence of these polar monomers improves the adhesion of the coating to the transparent film substrate or backing.

Preferred film forming polymers comprise at least two monomers selected from aliphatic alkyl (meth)acrylate monomers, bicyclic alkyl (meth)acrylates monomers and aromatic (meth)acrylates.

In one preferred embodiment of the invention especially useful with color copiers, the nonporous opaque thin film layer is selected such that the projected color image has an increase in pastel haze in regions of the image overlying the nonporous opaque thin film layer of no more than 10% when compared to a similar reference sheet without a nonporous opaque thin film backing. This provides an imaged sheet having much better image color quality in the areas of the imaging sheet which overlay the opaque area when compared to a sheet having a more conventional removable paper backing for feed facilitation.

In a highly preferred embodiment for color copiers, the nonporous opaque thin film layer or stripe has a sufficient machine direction width to simulate a piece of paper to the copier sensor. The copier then processes the imaging sheets of the invention at the same speed as paper, and allows tray feeding of the imaging sheets. This is a great advantage in machines such as the "Canon CLC" series color copiers, which only allow single bypass feeding of transparent imaging sheets at one per minute. This occupies an operator continually during imaging of multiple sheets.

However, this embodiment of the invention, which preferably bears a nonporous opaque thin film layer having a machine direction width of at least 1.75 cm, preferably at least 1.9 cm, may be fed in the paper tray in these copiers, allowing several hundred imaging sheets to be imaged without an operator present, and causes the imaging sheets to be imaged at the much faster paper rate rather than at the slower bypass rate.

Preferred imaging coatings for use with color copiers include polyester resins, e.g., polyesters based on bisphenol A, such as ATLAC™382E, (also sold as ATLAC™R 32-629), available from Reichold Chemical as well as bisphenol A monomers and their derivatives, (e.g., the dipropylene glycol ether of bisphenol A). A suitable carrier binder such as Vitel® PE 222 polyester resin, available from The Goodyear Tire and Rubber Company, is also present when bisphenol A monomers or their derivatives are used to facilitate coating. The thickness of this imaging coating is preferably between 0.5 to 10 µm, more preferably from 1 to 6.5 µm.

Where use in color copiers is desirable, the imaging coating may also contain polymeric, silica or starch particles to reduce pooling of the fusing oil at the edges of the sleeves and inhibit transfer of the oil to the stage of a projection device when the transparency is used. Useful particles are from 5 to 25 µm in diameter, more preferably from 10 to 20 µm in diameter. Larger particles are effective to reduce the oil pooling, but have the problem of being visible when projected. Smaller particles, i.e., less that 5 µm, in diameter may be used, but a higher loading is required to effectively reduce the oil pooling. This often results in higher haze of the final image. Also, the smaller particles are not effective in regions of the transparency where the thickness of the toner layer exceeds the extent to which the particles normally protrude from the imaging layer. This is especially important when multiple toner layers are present, e.g., in color electrophotography. For example, after fusing a two layer green (cyan plus yellow) toner layer on a Canon CLC 200, the toner thickness can be from 3.5 to 11 µm.

Preferred particles include Syloid® 620 particles, available from Davison Chemical.

When it is desirable to use the transparency with an ink-jet printer, the imaging coating the ink-receptive layer comprises a crosslinked semi-interpenetrating network, hereinafter referred to as an SIPN, formed from polymer blends comprising a) at least one crosslinkable polymeric component, b) at least one liquid-absorbent polymer comprising a water-absorbent polymer, and (c) optionally, a crosslinking agent. The SIPNs are continuous networks wherein the crosslinked polymer forms a continuous matrix. The SIPN is generated by crosslinking a copolymer containing from 3 to 20% ammonium acrylate groups with a crosslinking agent and then combining the copolymer with a liquid absorbent polymer or an uncrosslinked blend of the polymer.

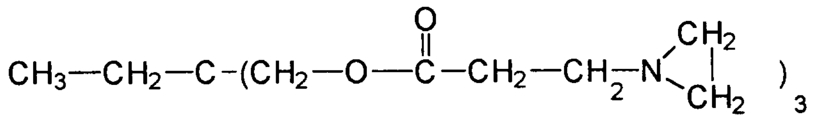
Such crosslinked systems have advantages for dry time, as disclosed in U.S. Patent 5,134,198 (Iqbal).

The water-absorbing hydrophilic polymeric material comprises homopolymers or copolymers of monomeric units selected from vinyl lactams, alkyl tertiary amino alkyl acrylates or methacrylates, alkyl quaternary amino alkyl acrylates or methacrylates, 2-vinylpyridine and 4-vinylpyridine. Polymerization of these monomers can be conducted by free-radical techniques with conditions such as time, temperature, proportions of monomeric units, and the like, adjusted to obtain the desired properties of the final polymer.

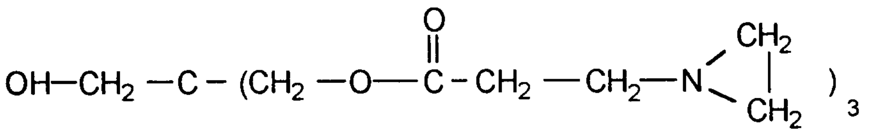
Hydrophobic polymeric materials are preferably derived from combinations of acrylic or other hydrophobic ethylenically unsaturated monomeric units copolymerized with monomeric units having acid functionality. The hydrophobic monomeric units are capable of forming water-insoluble polymers when polymerized alone, and contain no pendant alkyl groups having more than 10 carbon atoms. They also are capable of being copolymerized with at least one species of acid-functional monomeric unit.

Preferred hydrophobic monomeric units are preferably selected from certain acrylates and methacrylates, e.g., methyl(meth)acrylate, ethyl(meth)acrylate, acrylonitrile, styrene or α-methylstyrene, and vinyl acetate. Preferred acid functional monomeric units for polymerization with the hydrophobic monomeric units are acrylic acid and methacrylic acid in amounts of from 2% to 20%.

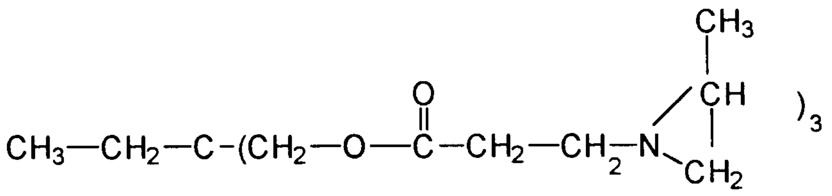
The crosslinking agent is preferably selected from the group of polyfunctional aziridines possessing at least two crosslinking sites per molecule, such as trimethylol propane-tris-(β-(N-aziridinyl)propionate)



pentaerythritol-tris-(β-(N-aziridinyl)propionate)



trimethylolpropane-tris-(β-(N-methylaziridinyl propionate)



and so on. Crosslinking can also be brought by means of metal ions, such as provided by multivalent metal ion salts, provided the composition containing the crosslinkable polymer is made from 80 to 99 parts by weight of monomer and from 1 to 20 parts by weight of a chelating compound.

SIPNs to be used for forming ink-receptive layers of the present invention typically comprise from 0.5 to 6.0 percent crosslinking agent, preferably from 1.0 to 4.5 percent, when crosslinking agents are needed. The crosslinkable polymer can comprise from 25 to 99 percent, preferably from 30 to 60 percent of the total SIPNs. The liquid-absorbent component can comprise from 1 to 75 percent, preferably from 40 to 70 percent of the total SIPNs.

Any imaging coating useful herein, e.g., whether designed for use with plain paper copiers, color copiers, or printers, may also contain polymeric particles. Useful polymeric particles range from 1 µm to 15 µm in diameter and include such polymers as poly(methylmethacrylate) (PMMA), modified poly(methylmethacrylate), poly(tetrafluorethylene), polyethylene, and particles produced from diol di(meth)acrylate homopolymers which impart antifriction characteristics when coated on image recording sheets. These diol di(meth)acrylates can be reacted with long-chain fatty alcohol esters of (meth)acrylic acid.

Preferred water based imaging coatings contain particles selected from PMMA, modified PMMA, and particles produced from diol-di(meth)acrylate homopolymers or copolymers of diol di(meth)acrylates reacted with long-chain fatty alcohol esters of (meth)acrylic acid.

Specifically such microspheres comprise at least 20 percent by weight polymerized diol di(meth)acrylate having a formula

$$CH_2{=}CR_2COOC_nH_{2n}OOCCR_2{=}CH_2$$

wherein R_2 is hydrogen or a methyl group, and n is an integer from 4 to 18. Examples of these monomers include those selected from the group consisting of 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,8-octanediol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, 1,12-dodecanediol di(meth)acrylate, 1,14-tetradecanediol di(meth)acrylate, and mixtures thereof.

Preferred monomers include those selected from the group consisting of 1,4-butanediol di(meth)acrylate, 1,6 hexanediol di(meth)acrylate, 1,12-dodecanediol di(meth)acrylate, and 1,14-tetradecanediol di(meth)acrylate.

The microspheres may contain up to 80 weight percent of at least one copolymerized vinyl monomer having the formula

$$CH_2{=}CR_2COOC_mH_{2m+1}$$

wherein R^2 is hydrogen or a methyl group and m is an integer of from 12 to 40.

Useful long-chain monomers include, but are not limited to lauryl (meth)acrylate, octadecyl (meth)acrylate, stearyl (meth)acrylate, and mixtures thereof, preferably stearyl (meth)acrylate.

The microspheres may optionally contain up to 30 percent by weight of at least one copolymerized ethylenically unsaturated monomer selected from the group consisting of vinyl esters such as vinyl acetate, vinyl propionate, and vinyl pivalate; acrylic esters such as methacrylate, cyclohexylacrylate, benzylacrylate, isobornyl acrylate, hydroxybutylacrylate and glycidyl acrylate; methacrylic esters such as methyl methacrylate, butyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, γ-methacryloxypropyl trimethoxysilane, and glycidyl methacrylate; styrene; vinyltoluene; α-methyl styrene, and mixtures thereof.

Most preferred microspheres include 50/50 poly(hexanediol-diacrylate/stearyl methacrylate), and 50/50 poly(butanediol-diacrylate)/lauryl(meth)acrylate, 80/20 poly(hexanediol-diacrylate)/stearyl(meth)acrylate, 50/50 polymethylmethacrylate/ 1,6 hexanedioldiacrylate, C_{14} dioldiacrylate, and C_{12} dioldi(meth)acrylate.

In addition to the above, useful microspheres may also comprise additives which are not ethylenically unsaturated, but which contain functional groups capable of reacting with materials containing reactive groups which may also be coated on the substrate along with the microspheres. Such additives are useful in modifying the degree of interaction or bonding between the microspheres and the imaging polymer. Suitable examples include organosilane coupling agents having alkyl groups with 1 to 8 carbon atoms, such as glycidoxy trimethoxysilanes such as γ-glycidoxypropyltrimethoxysilane, and (aminoalkylamino) alkyl trimethoxysilanes such as 3-(2-amino ethyl amino) propyl trimethoxysilane.

For good feedability, the mean particle size preferably ranges from 0.25 µm to 15 µm. Particles smaller than 0.25 µm would require the use of more particles to produce an effective coefficient of friction, this would tend to also produce more haze. Larger particles than 15 µm would require thicker coatings to anchor the particles firmly in the coatings, which would increase haze and coating cost. For good performance, the particles preferably have narrow particle size distributions, i.e., a standard deviation of up to 20% of the average particle size. These ranges are preferably 0.1-0.7 µm, 1-6 µm, 3-6 µm, 4-8 µm, 6-10 µm, 8-12 µm, 10-15 µm. More preferred particles are those having bimodal particle size distributions. This is made by mixing particles having 2 different particle size distributions. When bimodal particles are used, both particles can be selected from the preferred polymeric beads described above, or one of the particles can be a preferred microsphere and the other may be selected from other particles such as PMMA and polyethylene particles. If so, the second type of particle also preferably has a narrow particle size distribution.

Most preferably, both bimodal particles are selected from particles produced from the copolymer of hexanedioldiacrylate and stearylmethacrylate, having particle size distributions of from 1 to 4 µm and from 6 to 10 µm, or from 2 to 6 µm and from 8 to 12 µm, or from 0.20 to 0.5 µm and from 1-6 µm.

An antistatic agent may be present in any imaging coating. Useful agents are selected from the group consisting of nonionic antistatic agents, cationic agents, anionic agents, and fluorinated agents. Useful agents include such as those available under the trade name AMTER™, e.g., AMTER™ 110, 1002, 1003, 1006, and the like, derivatives of Jeffamine™ ED-4000, 900, 2000 with FX8 and FX10, available from 3M, Larostat™ 60A, and Markastat™ AL-14, available from Mazer Chemical Co., with the preferred antistatic agents being steramidopropyldimethyl-β-hydroxy-ethyl ammonium nitrate, available as Cyastat™ SN, N,N'-bis(2-hydroxyethyl)-N-(3'-dodecyloxy-2'2-hydroxylpropyl) methylammonium methylsulfate, available as Cyastat™ 609, both from American Cyanamid.

When the antistatic agent is present, amounts of up to 20% (solids/solids) may be used. Preferred amounts vary, depending on coating weight. When higher coating weights are used, 1-10% is preferred; when lower coating weights are used, 5-15% is preferred.

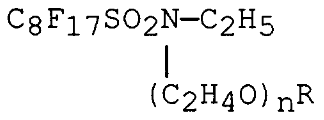
Where emulsion polymerization of the polymer is desired, an emulsifier is also present. The emulsifiers include nonionic, or anionic emulsifiers, and mixtures thereof, with nonionic emulsifiers being preferred. Suitable emulsifiers include those having a HLB of at least 10, preferably from 12 to 18.

Useful nonionic emulsifiers include C_{11} to C_{18} polyethylene oxide ethanol, such as Tergitol™, especially those designated series "S" from Union Carbide Corp., those available as Triton™ from Rohm and Haas Co., and the Tween™ series available from ICI America.

Useful anionic emulsifiers include sodium salts of alkyl sulfates, alkyl sulfonates, alkylether sulfates, oleate sulfates, alkylarylether sulfates, alkylaryl polyether sulfates, and the like. Commercially available examples include such as those available under the trade names Siponate™ and Siponic™ from Alcolac, Inc.

When used, the emulsifier is present at levels of from 1% to 7%, based on polymer, preferably from 2% to 5%.

Additional wetting agents with HLB values of from 7 to 10 may be present in the emulsion to improve coatability. These additional surfactants are added after polymerization is complete, prior to coating onto the polymeric substrate. Preferred additional wetting agents include fluorochemical surfactants such as



$$\begin{array}{l} C_8F_{17}SO_2N\text{—}C_2H_5 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad (C_2H_4O)_nR \end{array}$$

wherein n is from 6 to 15 and R can be hydrogen or methyl. Useful examples include FC-170C and FC-171, available from 3M. Another useful wetting agent is Triton™ X-100, available from Union Carbide.

Addition of a coalescing agent is also preferred for emulsion based coatings to insure that the coated material coalesces to form a continuous and integral layer and will not flake in conventional printing process. Compatible coalescing agents include propylcarbitol, the Carbitol™ series, as well as the Cellusolve™ series, and Propasolve™ series, from Union Carbide, and the Ektasolve™ series, available from Eastman Chemical. Other useful agents include the acetate series from Eastman Chemicals Inc., the Dowanol™ E series, Dowanol™ E acetate series, Dowanol™ PM series and their acetate series from Dow Chemical, N-methyl-2-pyrrolidone from GAF, and 3-hydroxy-2,2,4-trimethyl pentyl isobutryate, available as Texanol™, from Eastman Chemicals Inc. These coalescing agents can be used singly or as a mixture.

Other optional ingredients may be present in the imaging coating. Useful additives include such as crosslinking agents, catalysts, thickeners, adhesion promoters, glycols, defoamers and the like.

The desired imaging coating formulation can be prepared by dissolving the components in a common solvent, or dispersing therein in the case of a latex. Well-known methods for selecting a common solvent make use of Hansen parameters, as described in U.S. 4,935,307.

The imaging layer can be applied to the film backing by any conventional coating technique, e.g., deposition from a solution or dispersion of the resins in a solvent or aqueous medium, or blend thereof, by means of such processes as Meyer bar coating, knife coating, reverse roll coating, rotogravure coating, extrusion coating, and the like.

Drying of the imaging layer can be effected by conventional drying techniques, e.g., by heating in a hot air oven at a temperature appropriate for the specific film backing and coating chosen.

The imaging sheet of the invention may also comprise an ink-permeable protective layer such as polyvinyl alcohol, and the like, to insure faster drying.

Film substrates may be formed from any polymer capable of forming a self-supporting sheet, e.g., films of cellulose esters such as cellulose triacetate or diacetate, polystyrene, polyamides, vinyl chloride polymers and copolymers, polyolefin and polyallomer polymers and copolymers, polysulfones, polycarbonates, polyesters, and blends thereof. Suitable films may be produced from polyesters obtained by condensing one or more dicarboxylic acids or their lower alkyl diesters in which the alkyl group contains up to 6 carbon atoms, e.g., terephthalic acid, isophthalic, phthalic, 2,5-, 2,6-, and 2,7-naphthalene dicarboxylic acid, succinic acid, sebacic acid, adipic acid, azelaic acid, with one or more glycols such as ethylene glycol, 1,3-propanediol, 1,4-butanediol, and the like.

Preferred film substrates for the imaging sheet are cellulose triacetate or cellulose diacetate, polyesters, especially polyethylene terephthalate, and polystyrene films. Polyethylene terephthalate is most preferred. It is preferred that film substrates have a caliper ranging from 50 µm to 150 µm. Films having a caliper of less than 50 µm are difficult to handle using conventional methods for graphic materials. Films having calipers over 150 µm are very stiff, and present feeding difficulties in certain commercially available copying machines.

When polyester film substrates are used, they can be biaxially oriented to impart molecular orientation before the imaging layer is coated thereon, and may also be heat set for dimensional stability during fusion of the image to the support. These films may be produced by any conventional extrusion method.

In some embodiments, the polyester film forming the imaging sheet is extruded or cast, and uniaxially oriented in the machine direction. The imaging layer is then coated thereon. The composite can then undergo further orientation in the transverse direction to produce a finished product. When this process is used, the coated layer exhibits evidence of such stretching under optical microscopy, but surprisingly, the coating remains transparent, and the polymer, whether emulsion or solution polymerized, exists in a continuous coated layer without voids, thus showing the high integrity and cohesiveness of the coated layer. In these embodiments, the nonporous opaque thin film layer may be coated before or after orientation, but if coated before orientation, the film layer must be chosen such that it can withstand the subsequent processing without adverse affects.

To promote adhesion of the imaging layer to the film substrate, it may be desirable to treat the surface of the film substrate with one or more primers, in single or multiple layers. Useful primers include those known to have a swelling effect on the substrate polymer. Examples include halogenated phenols dissolved in organic solvents. Alternatively, the surface of the film substrate may be modified by treatment such as corona treatment or plasma treatment.

The primer layer, when used, should be relatively thin, e.g., preferably less than 2 µm, most preferably less than 1 µm, and may be coated by conventional coating methods.

Imaging sheets or "transparencies" of the invention are particularly useful in the production of imaged transparencies for viewing in a transmission mode or a reflective mode, i.e., in association with an overhead projector.

The following examples are for illustrative purposes only, and are not meant to be limiting. One skilled in the art will easily think of variations within the scope of the invention, which is solely that defined by the claims.

Test Methods

Image Transparency

Image transparency or "Pastel Haze" measures how much light is scattered by a fused toner layer. Higher quality images have lower pastel haze values. The haze of a yellow halftone was measured using a Gardner Model XL-211 Hazeguard hazemeter. First, the machine is zeroed with no film in place, the Reference/Open switch set to "Open". Next, the film is placed at the entrance port, and set the switch to "Reference" and record the reading. Again set the Ref/Open switch to "Open" and record reading. The percent Haze is computed according to the following formula.

Image Transparency

$$\% \text{ Haze} = \frac{(\text{Open Reading} \times 100\%)}{\text{Reference Reading}}$$

Increased Pastel Haze (Δ Pastel Haze) is determined by first determining the Pastel Haze of a reference film having no overlaid layer of any type. The Pastel Haze of overlaid films is then measured, and the Pastel Haze value of the reference film is subtracted therefrom to determine the Δ Pastel Haze.

Tensile Energy to Break

The Tensile Energy to Break is defined using the procedure of ASTM D882-91. A constant rate of grip separation method is employed. The rate of grip separation for all samples was 20 inch/minute. The sample length was approximately 4 inches. The initial spacing between grips was 2 inches, so the initial strain rate was (20 in/min)/(2 in)= 10/min.

While ASTM D882-91 defines Tensile Energy to Break as the energy per unit of volume to pull a sample to failure, this quantity is not useful in this application. The volume (i.e. thickness) of a particular sample is critically important to the sample's performance. We define Tensile Energy to Break as the integral under the stress/strain curve, WITHOUT dividing by the original volume.

Opacity Measurement

The opacity was measured using a Photovolt Model 575 Reflection Meter. The procedure is fully described in the user's manual.

1) The reference is set by turning the REF knob until neither the HI nor the LO light is lit.
2) The zero is set by placing a black standard over the opening, turning the COARSE sensitivity knob fully clockwise and setting the FINE sensitivity knob at it's midpoint. The ZERO knob is then adjusted until the PERCENT REFLECTANCE shows 00.0.
3) The sample to be measured is placed over the white reflection standard (furnished by the manufacturer for opacity measurements.) The sensor unit is placed on top of the sample and the sensitivity is set to 100%.
4) The sample is then placed on the black reflection standard (black felt) and the sensor placed on top of the sample. The value shown by the unit is the opacity.

Allowable Stack Height

Because striped film is thicker on the striped edge, a stack of film develops a wedge shape as the number of sheets increases. Thus as the wedge develops, part of the gravitational force (F_{slip}) acts in the direction down the slope, and so there is a tendency for the film to slip down the "slope" of the wedge. Frictional forces ($F_{friction}$)between sheets resist slippage, but as the stack height increases, the wedge angle (α) reaches a critical value (α_{crit}) the frictional force is overcome and the sheets begin to slide. This is illustrated in Figures 1 and 2. The film will slip at lower angles if the stack is jarred or subjected to vibrations. Both of these are common in copying machines. Figure 3 shows the force of gravity resolved into two forces, one normal to the plane of the film (F_{normal}), and one parallel to the plane of the film (F_{slip}). At wedge angles up to the critical angle the normal force is balanced by a reaction force applied by the underlying sheet. The slipping force is balanced by a frictional force whose magnitude is equal to the slipping force. At the critical angle the film is on the verge of slipping and the magnitude of the frictional force is: $F_{friction} = \mu_{static}\, mg \cos(\alpha_{crit})$. This is shown in Figure 4.

The height mismatch of the striped side to the unstriped side is determined by the thickness of the stripe (*t*) and the number of sheets. To a first approximation, the angle α can be calculated by treating the width (*w*) of the film as the hypotenuse and then calculating the height mismatch (*h*) as:

$$h = (\#sheets)^*(t)$$

Thus from Figure 5:

$$\alpha = \sin^{-1}(h/w)$$

And the maximum number of sheets (*Allowable Stack Height)* in a stack is given by:

$$\alpha_{crit} = \sin^{-1}[(\#sheets_{max})^* t/w]$$

or:

$$\#sheets_{max} = \sin(\alpha_{crit})^* w/t$$

For a given transparency film the quantity $\sin(\alpha_{crit})^* w$ is a constant, so the maximum number of sheets is inversely proportional to stripe thickness. For 3M PP2200 transparency film, the maximum number of sheets that can be stacked is approximately 100, $w = 215.9$ mm, and $t = 0.108$ mm. From the definition, $\alpha_{crit} = 2.8°$, and $\sin(\alpha_{crit})^* w = 10.8\ mm$.

The *Allowable Stack Height* was calculated based on the above equation with the data from PP2200 transparency film.

Examples

Example 1

An opaque, thin stripe was formed by coating a white coating having a thickness of 3.25 µm (0.13 mil) onto 10 µm (0.42 mil) PET film and slitting the film to 3.15 cm (1.25 inch) width in the machine direction. The thickness and the opacity of the stripe were measured. The Tensile Energy to Break of this stripe was determined. All of these measurements are summarized in Table 1.

A spray coating of #6065 adhesive, available from Minnesota Mining and Manufacturing Company (3M) was applied to the stripe. A transparency film was prepared by applying the coatings of 3M PP2270 Transparency film to 75 µm (3 mil) PET backing. The thin stripe was applied to the transparency film and imaged in a Canon CLC 200 copier. The stripe had a sufficient machine direction width to simulate a paper sheet, allowing tray feeding. The stripe was removed and the Pastel Haze of a part of the image that overlay the stripe was measured. The image quality of the same portion of the image was noted upon projection. The results of the imaging are summarized in Table 1.

Example 2

An opaque, thin stripe was formed by slitting 3M 25 µm (1 mil) TiO_2 filled PET film to 2.54 cm width. Processing and testing was done as in Example 1, and the results are summarized in Table 1.

Comparative Example 3C

An opaque, thin stripe was formed by slitting 3M 50 µm (2 mil) TiO_2 filled PET film to 2.54 cm width. Processing and testing was done as in Example 1, and the results are summarized in Table 1.

Comparative Example 4C

An opaque stripe was formed by slitting 3M 100 µm (4 mil) TiO_2 filled PET film to a 2.54 cm width. Processing and testing was done as in Example 1, and the results are summarized in Table 1.

Comparative Example 5C

A thin stripe was formed by slitting Dietzgen 340-M graph paper to 2.54 cm width. Processing and testing was done as in Example 1, and the results are summarized in Table 1.

This Example demonstrates that when porous materials such as paper are formed thin enough to attempt to minimize stacking variation, that the tensile strength, and opacity decrease drastically while the insulative effect decreases more slowly. As shown in Table 1, the strength to break is drastically reduced, 0.07 joule, which would not be cleanly removable; the opacity is also inadequate at 62% and the image quality is poor due to the insulative properties remaining.

Comparative Example 6C

A stripe was formed by slitting the paper backing of 3M PP2410 transparency film to a 2.54 cm width. Processing and testing was done as in Example 1, and the results are summarized in Table 1. This Example uses the same paper as Examples 4 and 11-13 of U. S. Patent 5,208,093 in the original thickness.

This Example demonstrates that porous materials used in typical thickness have 888

Reference Example 7

A sample of the transparency film described in Example 1 was prepared to serve as a reference. The pastel haze of an identical image not overlying the stripe was measured and image quality noted.

Table 1

Example No.	Stripe Thickness (μm)	Stripe Opacity (%)	Tensile Energy to Break (joules)	Δ Pastel Haze (%)	Image Quality
1	12.7	72.9	4.98	5.6	very good
2	22.9	79.9	10.52	9.3	good
3C	45.7	92.7	1.20	30.7	poor
4C	106.7	95.4	7.46	69.4	poor
5C	45.7	62.0	0.07	45.4	poor
6C	81.3	85.0	0.09	61.9	poor
7	-	-	-	Ref.	very good

Example 8

An opaque, thin stripe was formed as in Example 1. A UV cured acrylic hot melt adhesive was applied to the stripe and the stripe was laminated to 3M PP2500 Transparency Film. The average film thickness, the average thickness of the striped part of the film, and the Thickness Ratio are tabulated in Table 2. Six hundred sheets of this film were loaded at one time in a Xerox 1090 copier. The sheets fed and imaged reliably. The stripe was easily removed without tearing even over a wide range of removal speeds and geometries.

Example 9

A striped film was made by using the stripe material and adhesive from Example 1 and adhering it to 3M PP2500. The average film thickness, the thickness of the striped part of the film, and the Thickness Ratio are tabulated in Table 2. The Allowable Stack Height is calculated and tabulated in Table 2. The stripe was easily removed without tearing even over a wide range of removal speeds and geometries.

Example 10

A striped film was made by using the stripe material and adhesive from Example 2 and adhering it to 3M PP2500. The average film thickness, the thickness of the striped part of the film, and the Thickness Ratio are tabulated in Table 2. The Allowable Stack Height is calculated and tabulated in Table 2. The stripe was easily removed without tearing even over a wide range of removal speeds and geometries.

Comparative Example 11C

A striped film was made by using the stripe material and adhesive from Comparative Example 3C and adhering it to 3M PP2500. The average film thickness, the thickness of the striped part of the film, and the Thickness Ratio are tabulated in Table 2. The Allowable Stack Height is calculated and tabulated in Table 2. The stripe was easily removed without tearing even over a wide range of removal speeds and geometries.

Comparative Example 12C

A striped film was made by using the stripe material and adhesive from Example 4 and adhering it to 3M PP2500. The average film thickness, the thickness of the striped part of the film, and the Thickness Ratio are tabulated in Table 2. The Allowable Stack Height is calculated and tabulated in Table 2. The stripe was easily removed without tearing.

Comparative Example 13C

A striped film was made by using the stripe material and adhesive from Example 5 and adhering it to 3M PP2500. The average film thickness, the thickness of the striped part of the film, and the Thickness Ratio are tabulated in Table 2. The Allowable Stack Height is calculated and tabulated in Table 2. The stripe had to be removed carefully to prevent tearing.

Comparative Example 14C

A striped film was made by using the stripe material and adhesive from Example 6 and adhering it to 3M PP2500. The average film thickness, the thickness of the striped part of the film, and the Thickness Ratio are tabulated in Table 2. The Allowable Stack Height is calculated and tabulated in Table 2. The stripe had to be removed carefully to prevent tearing.

Reference Example 15

3M PP2200 Paper Striped Transparency Film was used as a reference example of a striped film. The average film thickness, the thickness of the striped part of the film, and the Thickness Ratio are tabulated in Table 2. The Allowable Stack Height is calculated and tabulated in Table 2. The stripe had to be removed carefully to prevent tearing.

This Example uses the same paper as Examples 1-3 and 5-10 of U. S. Patent 5,208,093 in the original thickness.

Table 2

Example No.	Average Film Thickness (μm)	Striped Film Thickness (μm)	Thickness Ratio	Allowed Stack Height (No. sheets)
8	98.6	119.6	1.21	524
9	98.6	121.5	1.23	478
10	98.6	129.1	1.31	355
11C	98.6	154.5	1.57	193
12C	98.6	215.4	2.18	93
13C	98.6	153.2	1.55	200
14C	98.6	185.0	1.88	125
15	98.6	206.8	2.10	100

Example 16

An opaque, thin stripe was formed by taking a composition comprising Atlac 382E, 4 g, dissolved in 6 g of a 50/50 weight/weight MEK/Toluene mix, into which had been dispersed 2 g of TiO_2 pigment, and coating it 150 μm (6 mils) wet on unprimed Mylar PET film. When dry, the coating could be removed by adhering a strip of Filament Tape and pulling. The coating came away as a coherent strip. This illustrates use of an organic solvent formulation.

Example 17

Examples 17-20 demonstrate the removability of a printed layer coated directly onto the imaging sheet. The thickness of the dry coating thickness ranges from 10% to 33% of the wet thicknesses mentioned, depending on the percent solids of the coating solution made. These examples are provided simply to exhibit removability or lack thereof for a variety of coatings. Opaque layers coated in this manner must be within the thickness range claimed in order to provide the imaging benefits previously described. The coatings were tested for removeability by lifting a corner with masking tape, and filament tape. The former removes coatings with relatively low adhesion, and the latter removes coatings with higher adhesions. Coatings not removable with filament tape are considered useless for this application.

A 33% solution of poly(vinylpyrrolidone), grade K17, considered a low viscosity grade, had dispersed in it 4 g of TiO_2 pigment. This was coated at 150 µm (6 mils) wet thickness, on a variety of substrates and air dried.

Table 3

Substrate	Removeability
Unprimed Mylar PET	Clean removal with Masking Tape
Polyester N2 primed	Poor removal, even with Filament Tape
PP2500, improved	95% removal with Masking Tape; 100% removal with Filament Tape
PP2500, original	No removal with Filament Tape
Polyester, PVDC prime	30% removal with Masking Tape; 75% removal with Filament Tape

An addition to the above formulation of 2 drops of a 10% solution of FC190C, a Fluorocarbon surfactant, and coating as above on unprimed Mylar produced a smoother coating that was easier to remove.

This example illustrates the effect of the substrate treatment on the coated layer removal, and the improvements that may be brought by minor additives.

Example 18

1 gram of TiO_2 pigment was dispersed in 10 g of a 20% gelatin solution. The composition was coated at 40°C, 250 µm (10 mils) wet onto 100 µm (4 mil) unprimed PET film. When dry, a corner could be lifted with a finger nail, and the whole film removed as an integral layer. It was noticed that the dryness of the coating influenced the adhesion to the film, suggesting that the addition of a humectant could be used to control adhesion properties.

Example 19

A variety of commercially available poly vinylalcohols were coated, without pigment, onto unprimed PET, and the dried film tested for peelability. Among the materials examined were Airvol™ and Gohsenol™ products. It was observed that the coatings when removed exhibited "static cling", and it is anticipated that an antistatic agent, such as a Cyastat™ SN or 609, available from American Cyanimid would reduce or eliminate this problem.

Example 20

8 g of Gohsenol KP06, a commercial polyvinylalcohol were dissolved in 28 ml of water, and subsequently, 4 g TiO_2 dispersed in that solution. This formulation was a thick, slow-flowing paste, somewhat like a lithography ink. It was coated 250 µm (10 mils) thick onto 100 µm (4 mil) unprimed PET using a Baker Bar coater. When dry, the coating had an opacity of 72.3%, as measured with a Photovolt unit, and could be cleanly peeled with Masking Tape, or by loosening a corner carefully and pulling.

Example 21

Composite imageable sheets were prepared by applying an opaque stripe 2.54 cm wide to a sheet of 3M PP2500 transparency film, and then cutting the stripe so that the final machine direction width of the stripe was 1.9 cm. The films were fed in Canon CLC 200 and Xerox 5765 color copiers. In each case the 1.9 cm stripe was sufficient in machine direction width to simulate a paper sheet, and the film was fused at the paper speed.

Samples of identical 3M PP2200 film bearing a 1.4 cm machine direction width stripe were fed into the Canon CLC 200 and Xerox 5765 color copiers, and were not sufficient to simulate a paper sheet in the copiers. The films were fused at (the slower) transparency speed.

Claims

1. A composite imaging sheet for use in copying and printing machines comprising a transparent imageable sheet having a machine direction and a transverse direction, said sheet having two major surfaces, each surface having four edges having edge portions, said sheet bearing a releasable thin opaque film layer having a total thickness of from 5 µm to 60 µm and a film thickness of no greater than 30 µm on at least one edge portion of one major surface of said imageable sheet, said thin film layer having an opacity of at least 70%, and a tensile energy to break of at least 0.1 joule.

2. A composite imaging sheet according to claim 1 wherein said nonporous opaque thin film layer is formed from a material selected from the group consisting of polyolefins, polybutylene, polystyrene, polyesters, polymethylmethacrylate, cellulose acetate, polyvinylchloride, polyvinylidiene fluoride, polyamides, polyimides, and mixtures thereof.

3. A composite imaging sheet according to claim 2 wherein said nonporous opaque thin film layer is formed from a material selected from the group consisting of polyethylene, and poly(ethylene terephthalate).

4. A composite imaging sheet according to claim 1, said film layer being releaseably attached to said edge portion by means of an adhesive.

5. A composite imaging sheet according to claim 1, said film layer having been directly coated onto said edge portion of said major surface.

6. A composite imaging sheet according to claim 4 wherein said adhesive composition comprises:

   a) from 50 to 90 parts by weight of at least one lower alkyl acrylate having an alkyl group comprising from 4 to 12 carbon atoms; and
   b) from 10 to 50 parts by weight of at least one higher alkylacrylate having an alkyl group comprising from 12 to 26 carbon atoms.

7. A composite imaging sheet according to claim 1 wherein said nonporous opaque thin film layer has a film thickness of from 5 µm to 30 µm, and said thickness of said adhesive layer ranges from 5 µm to 15 µm.

8. A composite imaging sheet according to claim 1, said imaging sheet being suitable for use in a color copier, wherein a color image on said imaging sheet will, when projected, exhibit an increase in pastel haze of less than 10% in regions of the image overlying the strip, when compared to a reference sheet having no nonporous opaque thin film layer.

9. A composite imaging sheet for use in copying and printing machines comprising a transparent imageable sheet having a machine direction and a transverse direction, said sheet having two major surfaces, each surface having four edges having edge portions, said sheet bearing a releasable thin opaque film layer having a total thickness of from 5 µm to 60 µm and a film thickness of no greater than 30 µm on at least one edge portion of one major surface of said imageable sheet, said nonporous opaque thin film layer having a tensile energy to break of at least 0.1 joule, wherein said nonporous opaque thin film layer varies in opacity along a gradient in said transverse direction from 75% to less than 35%..

10. A composite imaging sheet according to claim 1 bearing a nonporous opaque thin film layer on multiple edge portions of a major surface said sheet.

11. A composite imaging sheet according to claim 1 wherein said nonporous opaque thin film layer is formed from a pigment-filled composition having a pigment to binder ratio being preferably less than one.

12. A composite imaging sheet according to claim 1 wherein said nonporous opaque thin film layer has a sufficient machine direction width to simulate a piece of paper in said copying machine, said width being at least 1.75 cm.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 11 0623

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.6)
A	WO-A-92 17822 (MINNESOTA MINING AND MANUFACTURING) * page 8, line 26 - line 37; examples 2,3 * ---	1-12	G03G7/00
A	WO-A-93 13460 (MINNESOTA MINING AND MANUFACTURING) * claim 1 * ---	6	
A	US-A-4 873 135 (B WITTNEBEL ET AL) * the whole document * ---	1-12	
A	EP-A-0 570 740 (CANON) * page 7, line 5 - line 29; claim 1 * ---	1-12	
A	DE-A-42 42 249 (RENKER) * the whole document * ---	1-12	
A	PATENT ABSTRACTS OF JAPAN vol. 7 no. 192 (P-218) ,28 August 1983 & JP-A-58 090647 (FUJI XEROX) 30 May 1983, * abstract * -----	1-12	TECHNICAL FIELDS SEARCHED (Int.Cl.6) G03G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23 November 1995	Heywood, C

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