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㊿ Method for making direct negatives and direct masters by electroerosion recording.

(57) An electoerosion recording medium for generation of direct negatives or direct masters comprises a conventional support on which is deposited a thin conductive layer, and a protective overlayer comprising a crosslinked binder. The overlayer contains a solid conductive lubricant and optionally a particulate scouring agent to inhibit electrode fouling during writing. Preferably a hard base layer is present between the support and the conductive layer.

The specification describes a method of making a direct negative or direct offset by an electroerosion process using the foregoing recording medium, said method comprising selectively electro-eroding the conductive layer and thereby selectively simultaneously removing the crosslinked polymer layer.

Croydon Printing Company Ltd.

METHOD FOR MAKING DIRECT NEGATIVES AND DIRECT MASTERS BY ELECTROEROSION RECORDING

The present invention relates to a method for making direct negatives and direct masters by electroerosion recording and products so formed.

Electroerosion printing is a well known technique for producing markings such as letters, numbers, symbols, patterns, such as circuit patterns or other legible or coated indicia, on a recording material in response to an electric signal which removes or erodes material from the surface of the recording material as the result of spark initiation.

The surface which is locally removed during writing to provide such indicia on the recording material is usually a thin film of a conductive material which is vaporized in response to localized heating associated with sparking (arcing) initiated by applying an electric current to a stylus, multiple styli or electrodes (electrode and stylus are used interchangeably herein) in contact with the surface of the recording material comprising the thin conductive film on a non-conductive backing or support. In the present state of the art, the thin conductive film is usually a thin vacuum-deposited film of a vaporizable metal, such as aluminum.

The electroerosion printing is effected by movement of the electrode (or a plurality of electrodes) relative to the surface of the electroerosion recording media while maintaining good electrical contact between the styli tips and the aluminum overlayer. Electrical writing signals are fed to the electrode to provide controlled electrical pulses which generate sparks at the surface of the recording material to selectively heat and remove, by evaporation, a layer of the recording material; the locations from which material is removed correspond to the indicia or images which are to be recorded.

Electroerosion recording materials and processes are useful to directly produce human readable images, photomasks, etc. Substrates of paper and various polymers have been employed with thicknesses on the order of 2 to 5 mils; as the erodible conductive layer, metal films such as vapor deposited aluminum films having a thickness on the order of 100 Å to 1,000 Å have been utilized. For details on such materials heretofore used in electroerosion printing see also U.S. Patent 4,082,902 Suzuki and U.S. Patent 4,086,853 Figov.

When using a metallized polyester sheet as a medium for electroerosion printing with a multistylus head where the pressure on the individual styli may vary, due to the fragility of the thin conductive layer severe mechanical scratching has been observed. This results in unsatisfactory print quality and a poor quality direct negative due to light transmission in the scratched areas. It is believed that the scratching is attributable to several causes, including plastic deformation of the substrate during writing. The thin conductive film, for example, the vapor-deposited thin aluminum film, apparently cannot withstand the high strains generated when the support or substrate is deformed and therefore ruptures resulting in scratching. Also there are occasions when the styli cold-weld to the thin aluminum conductive layer so that the structure suffers shear either at the aluminum-substrate interface or below it in the substrate itself.

It has been recognized for sometime, therefor, that the use of a lubricant and/or protective overcoat on the surface of an electroerosion recording material would be helpful to reduce scratching by the electrode.

The prior art has utilized lubricants comprising long chain fatty acids, e.g., lauric, stearic and arachidic acids, and silicone oils. However, even with the use of such lubricants, some electrode scratching of the removable layer of the electroerosion recording material was observed. Accordingly, efforts continue to be directed to finding a superior lubricant and/or protective layer composition for the surface of electroerosion recording materials.

It has also been observed that in addition to the use of a lubricant overlayer, when a thin, hard underlayer is formed on the plastic substrate prior to metallization, scratching can be reduced to acceptable levels.

Several additional prior art patents relevant to electroerosion recording or printing are discussed below.

U.S. Patent 2,983,220 Dalton et al discloses a lithographic coating on an electroerosion recording sheet. The coating may be a ZnO or ZnS pigmented copolymer binder system.

A layer containing a conductive material, such as graphite, is disclosed in U.S. Patent 3,048,515 Dalton.

An electroresponsive recording blank having a removable masking layer containing a luminescent material is disclosed in U.S. Patent 2,554,017 Dalton.

Other prior art providing further general background in the field of electroerosion printing includes U.S. Patent 3,138,547 Clark and U.S. Patent 3,411,948 Reis.

High temperature lubricants comprising graphite in oil are also known as is disclosed in U.S. Patent 3,242,075 Hunter.

U.S. Patent 3,514,325, Davis et al, discloses an electroerosion recording material in which a surface layer of crosslinked binder containing conductive particles such as zinc oxide is placed on top of the thin aluminum layer to achieve improved resistance to surface abrasion from a surface-contacting writing electrode.

U.S. Patent 3,740,254, Lansbury et al, describes an isocyanate-ended polyurethane composition, i.e., a prepolymer, as a primer for the deposition of thin aluminum films on various substrates including plastic substrates. The purpose here is to improve adhesion of the aluminum film.

U.S. Patent 3,786,518, Atherton, describes an electroerosion recording material comprising, for example, a thin conductive film of aluminum deposited over a resin which has been provided with a matte finish by the inclusion of a matting agent or by treating the resin surface. A wide variety of resinous materials is suggested for the resin layer.

U.S. Patent 4,268,570, Imanaka et al, describes the optional use of a polyurethane adhesive layer between the polymer support and the aluminum layer, optionally having a top coating of an acrylic resin, a urethane acrylate resin, or a polyester block copolymer resin, in plastic molded products, such as, resin plates, tubes, and the like. The structures are unrelated to electroerosion printing.

U.S. Patent 4,217,596, Jung, describes an electroerosion recording paper comprising a layer of lacquer or printing ink or both between the thin conductive aluminum layer and a paper support.

U.S. Patent 4,305,082, Kusakawa et al, describes an electroerosion recording paper in which a resistance layer may be provided over a thin conductive aluminum film.

U.S. Patent 4,304,806, Anderson et al, describes information-carrying discs coated with an abrasion-resistant polymer layer derived from an epoxy-terminated silane.

U.S. Patent 4,339,758 Bhatia et al, describes an electrosensitive recording that uses a silicon dioxide containing resinous base layer between a support and an overlying metallic film.

A lithographic plate must consist of two kinds of areas: printing areas, which accept grease (ink) and repel water, and non-printing areas, which accept water and repel grease (ink). The wider the difference between the ink accepting activity of the image and the water accepting and ink repelling activity of the non-image areas, the better the print quality when the plate is run on the press.

IN EP-A-113005 a method for making high contrast, scratch-free direct negatives and short run offset masters is disclosed. According to this method, the electroerosion recording material comprises a thin, hard hydrophobic base layer between a transparent polymer support and an aluminum layer and a graphite-containing overlayer which is also hydrophobic. In the use of this material as a direct master, the necessary hydrophilic/hydrophobic mapping is accomplished by removing the overlayer with a suitable solvent subsequent to electroerosion printing, whereby a substantial number of copies can be made before the aluminum layer starts to wear away.

There is no prior art that provides a method for making sufficiently wear-resistant electroerosion recording materials such that a direct master for making a substantial number of copies can be formed with ultimate simplification of the process for making the same.

SUMMARY OF THE INVENTION

In a method of making direct negatives or direct offset masters (often merely a "direct master" herein) by an electroerosion technique, a crosslinked protective overlayer is provided which comprises a solid conductive lubricant, e.g., graphite in a crosslinked polymer matrix with or without a particulate material such as silica or alumina which serves as a scouring agent, thereby providing a scouring action to inhibit electrode fouling during the printing process.

One object of the present invention is to provide a recording material suitable for generation of wear-resistant direct negatives and long run direct masters by electroerosion printing.

A further object of the present invention is to provide an electroerosion recording material with a durable crosslinked protective overlayer which can be employed to generate direct masters that permit a plurality of copies to be obtained without the same wearing off the recording material.

A further object of the present invention is to provide an improved electroerosion recording material which includes a crosslinked protective overlayer that resists abrasion and mechanical scraping.

Another object of the invention is to provide overlayer compositions which also exhibit improved contrast when used to produce direct negatives by electroerosion printing. In such usage a dark polymer film, e.g., a dark graphite/ crosslinked polymer film, serves to help block light that may be partially transmitted through the thin conductive film, e.g., a thin aluminum film.

A further object of the present invention is to provide a conductive crosslinked overlayer with improved adhesion to a thin conductive film, e.g., aluminum.

A further object of the present invention is to provide direct negatives or direct masters as above described which further comprise a hard polymeric base layer.

An advantage of the overlayers of this invention is that they are electrically conductive and therefore can be used in thicker layers than can insulating films.

The invention will now be further described with reference to the accompanying drawings, in which:

Fig. 1 of the drawings is a cross-sectional view of an electroerosion recording material in accordance with a preferred embodiment of this invention;

Fig. 2 is a cross-sectional view of a direct negative made in accordance with one embodiment this invention; and

Fig. 3 is a cross-sectional view of an offset master made in accordance with one embodiment this invention.

In Fig. 1 of the drawings, 1 indicates the support, e.g., a polyester.

The optional hard base layer of the present invention formed thereon is represented by numeral 2 and is shown between the support 1 and the conductive film 3.

The protective overlayer of the present invention 4 is shown deposited thereon.

In Fig. 2, a direct negative is shown formed after electroerosion printing wherein imaged regions 5 are shown where the conductive layer 3 and the protective overlayer 4 have been removed following electroerosion printing. Also shown are unwritten areas 6.

Fig. 3 shows an offset master formed per the present invention where unwritten area 6 as shown in Fig. 2 have been removed in a conventional manner, for example, by immersion in a solvent such as isopropanol, N-butanol, or conventional standard cleaning solutions for printing processes based on a water-dampering ink cycle. Typically, immersion is at room temperature and the abrasion resistant top coat is merely removed by swabbing the same.

The drawing is not to scale.

The Support

Examples of the support which can be employed for the electroerosion recording material of the present invention are not unduly limited in any fashion so long as the base layer applied thereon will adhere thereto and the support is dimensionally stable and has sufficient thermal as well as mechanical stability to permit use under widely varying conditions.

It is most preferred that the support of the present invention be a high optical quality polymer film, such as a transparent polyester film (Mylar ®). Other though useful materials include paper, polymers such as polyethylene terephthalate, Riston, Kapton, polycarbonates, polypropylenes, polyethylenes, etc. As will be appreciated by one skilled in the art, when the desired product is a direct master an opaque support is acceptable, in this instance the printed area being receptive to oil based inks. However, when a direct negative is the desired product, the support should be transparent (as should the hard base layer and fillers therin, when used).

The thickness of the support is not limited in any particular fashion so long as sufficient strength is provided to the direct negative or direct master during use. Typically, however, thicknesses will be on the order of about 1 mil to about 5 mils.

The Base Layer

While the base layer of the present invention is optional, the use thereof provides a most highly preferred embodiment of the present invention.

The optional thin, hard polymeric base layer may or may not be crosslinked. It should have a sufficiently high tensile strength and a sufficiently high softening temperature so that it reduces plastic deformation of the support during electoerosion so that scratching of the conductive film is minimized. With hard supports, e.g., polycarbonates, benefits from the use of a base layer are reduced. However, in general, the base layer provides superior results when it is present. Preferably the base layer contains an inorganic filler. Crosslinking the base layer is preferred since this generally provides a harder base layer, reducing the chance of generating a soft residue during electroerosion which might adhere to the electroerosion styli and inhibit writing. When a filler is used, e.g., to scour off debris, crosslinking firmly fixes the filler in place, reducing the chance of filler dislodgement and adherence to the electroerosion styli. In addition, a crosslinked base layer improves the corrosion resistance of the conductive film due to its good passivating properties, thus increasing shelf life and performance reliability.

The hard base layer is generally harder than Mylar®, preferably has a high Tg, for example, equal to or greater than 130°C, preferably has a hardness greater than 20 and more preferably greater than 30 (Knoops hardness), most preferably shows at least a 4 to 7% elongation at break (Tensile Instron) and when hydrophobic has a contact angle with water of equal to or greater than about 75°. If hydrophilic, it preferably has a contact angle with water of 30° or less.

The base layer is typically formed from solvent castable polymeric/oligomeric materials containing residual reactive sites such as free hydroxyl, epoxy, olefinic, acetylenic, α, β-unsaturated carbonyl moities, etc., which can most preferably be crosslinked by suitable reagents using heat and/ or radiation to accelerate the curing process. With these materials, crosslinking can also be accomplished by thermal or radiation-induced processes without the addition of another crosslinking agent.

Following are representative examples of various crosslinked polymer systems for application in the base layer according to this invention:

Urethane crosslinked cellulosic coatings with and without roughness causing particulate material are formed from cellulose derivatives and aromatic or aliphatic polyisocyanates, typically in the presence of suitable dispersing agents, catalysts and wetting agents well known to those skilled in the polyurethane art. Suitable cellulose derived materials include: cellulose acetate butyrate (CAB), ethyl cellulose (EC), nitrocellulose, cellulose acetate and cellulose diacetate, etc. Alternate materials containing unsubstituted hydroxyl groups for reaction with polyisocyanates to form crosslinked polyurethanes are: polyvinyl butryal, polyvinyl formal, Bakelite phenoxy resins, phenolic resins, e.g., novolaks (which have a slight color) epoxies such as Eponols and polyether glycols such as "Teracol" (from DuPont), and poly(sytrylallyl alcohol). Typical polyisocyanates that react with available -OH groups of cellulosic binders or alternate systems include toluene diisocyanate, diphenylmethane diisocyanate, hexamethylene diisocyanate-based systems such as Desmodur N-75 (aliphatic prepolymer, Mobay Chemical Co.) and

Mondur Resins such as CB-60 and CB-75, and Mondur HC. Melamine crosslinking agents can also be employed to obtain thermoset coatings with the above binders.

Inorganic fillers such as SiO_2, $CaCO_3$, TiO_2 and calcium silicate, etc., generally of a particle size ranging from 0.5 μm to 10 μm can be incorporated by the usual techniques of grinding or milling together with the binder, a urethane solvent such as a methyl ethyl ketone (MEK)-toluene mixture, and a suitable dispersing agent such as Multron R221-75, a saturated polyester resin from Mobay Chemical Co. Other useful solvents are the same as for overlayer formation later discussed.

The urethane forming reactions of the above described binders and urethane prepolymers are generally catalyzed by conventional organometallic reagents such as stannous oleate, stannous octoate, dibutyl-tin dioctoate, dibutyl-tin dilaurate, calcium or cobalt naphthenate, also tertiary amines, etc. Further acceleration of the crosslinking reaction can be achieved by thermal treatment of the coatings.

Crosslinked polymer coatings with beneficial properties can be obtained by the use of radiation curable acrylated polyurethane oligomers of the type "UVITHANE 783" and "UVITHANE 788" available from Thiokol Chemical Div. Inorganic fillers such as silica can be dispersed by conventional techniques prior to coating.

Highly crosslinked films can also be obtained by thermal or radiation-induced copolymerization/ co-crosslinking of the above UV curable urethane oligomers with added multifunctional monomers such as pentaerythritol triacrylate (PETA) and trimethylol-propane triacrylate (TMPTA) available from Celanese Corporation.

Desired crosslinked films with or without inorganic fillers can also be formed by thermal, microwave, or UV curing of coatings cast from blends of acrylated cellulosic derivatives and UV curable urethane oligomers described above.

Usually from about 0.5 to about 1.5 weight percent catalyst based on total organics weight (hereafter, same basis) provides good results.

Drying/curing is often at about 90 to about 110°C for about 5 to about 15 minutes. Higher and lower temperatures and times can be used.

For optimal performance in terms of faster curing within 3-5 minutes at 100°C or so base coat formulations were typically formed at an NCO:OH ratio of about 0.5 to about 1, more preferably 0.7 to 0.8.

The particulate solid filler, when used, and this is a highly preferred embodiment of the invention, is typically used in an amount of from about 3 to about 40 weight percent, more preferably from 5 to 25 weight percent, based on the weight of total organics present. Talysurf Traces of typical filled films show a peak to valley ratio on the order of 1 to 2 microns.

While not to be construed as limitative, typically the base layer has a thickness of from about 2 to about 10 μm.

The Conductive Layer

A conductive layer, typically of a metal such as aluminum, is formed on the base layer by a conventional technique such as sputtering or vacuum evaporation.

The only characteristic which the metal layer must exhibit is that upon application of an electrical pulse which results in an arc between the stylus and the metal layer, the same is cleanly eroded or vaporized with the protective layer thereover. If this criterion is met, any conductive material can be used in the present invention.

Useful metals include aluminum, magnesium, etc., typically formed by vacuum evaporation or sputtering in a conventional manner.

It is most preferred that the metal layer exhibit a resistivity ranging from about 0.5 to 5 ohms per square centimeter. The maximum conductivity is in no fashion limited.

The thickness of the conductive layer is not limited in any substantial fashion so long as it can be electroeroded. However, for optimum print quality at low voltage, typically the thickness will be on the order of about 100 Å to 1000 Å.

The Overlayer Comprising a Crosslinked Binder Matrix with a Conductive Solid Lubricant and Optional Scouring Agent

Applicants approach this aspect of the invention by firstly discussing the nature of the crosslinked polymer, nextly discussing the solid conductive lubricant incorporated therein and finally discussing the optional scouring agent which may be incorporated therein.

The overlayer can be hydrophobic or hydrophilic. Its hydrophobic or hydrophilic nature is not important when it is used in a direct negative. If used in a direct negative, it may be totally removed prior to use or it may be permitted to remain in unwritten areas. If hydrophobic, it should be removed if it is to be used in a direct master in a printing process involving oleophilic inks. As one skilled in the art will appreciate, the support or base layer, whichever is exposed following electroerosion, should have a wettability opposite the overlayer if the overlayer remains, if use as a direct master is contemplated, to ensure selective wetting and non-wetting by the inks use, specifically that written areas preferentially receive the ink. If direct master use is contemplated, conventional oleophilic or aqueous inks are used in a conventional manner. It is generally preferred to remove the unwritten areas of the protective overlayer, be it hydrophobic or hydrophilic, to avoid any possible smudging problem during use as a direct master. It will be appreciated by those skilled in the art that instead of the conventional oil-based ink, this technology is capable of being used with an aqueous ink provided that the electroerosion process and the nature of the overcoat and base layers are differently chosen so that the ink-receptive areas where printing is desired are hydrophilic, and the background areas where no ink is desired are hydrophobic.

The overlayer should be resistant to humidity to ensure a good shelf life, ease of shipping and ease of handling. If used in a direct master, it should, of course, be resistant to any materials used, e.g., water, oleophilic ink, etc., if it is not removed.

The most critical aspect of the overlayer of the present invention is that it be crosslinked so that the same will not come off the thin conductive layer during handling, etc., but the same can be removed in unwritten areas following electroerosion, if desired, by a simple procedure, such as solvent contact and swabbing.

A hydrophilic overlayer of the present invention should be resistant to the water cycle on a press during printing. It most desirably exhibits a contact angle with water of about 30° or less. As one skilled in the art will appreciate, oleophilic ink should not wet the hydrophilic overlayer. Further, it should be water insoluble but water wettable.

A hydrophobic overlayer per the present invention illustrates a contact angle with water of 75° or more.

The exact polymer selected for use in the present invention is not overly critical so long as it can be crosslinked to form a tough polymeric layer. A most desirable characteristic for the binder system is that it should form a stable dispersion with particulate materials such as graphite, ZnO, silica, alumina, etc.

It is most preferred that the polymer be crosslinked to a degree of from about 10 to about 50% (the percentage of the crosslinking sites on the hydrophilic binder which are crosslinked).

The degree of hydrophilicity of crosslinked hydrophilic polymer-particulate films used as the overlayer in the present invention should be such that the non-image areas of the print material with hydrophobic written regions have the ink-repelling property necessary for a direct master when using oleophilic inks in a conventional water-ink cycle on a printing press.

From the standpoint of process viability, the factors which dictate our selection of materials and processes for generation of the at least partially crosslinked hydrophilic polymer layer include:

(a) Solubility of starting materials so that these can be applied from solution in commonly employed solvents and the resulting coatings can be cured/crosslinked within minutes at temperatures not exceeding 120°C.

(b) The cured films must be tack-free so as to eliminate the possibility of blocking on storage in roll form.

(c) The polymer binders should be compatible with solid lubricants and inorganic fillers as later described to obtain stable dispersions and homogeneous coatings.

(d) Formulations containing binder-crosslinking agent-filler combinations should have the necessary pot life desired for a particular coating environment.

Hydrophilic polymers which can be crosslinked per the present invention include but are not limited to polyvinyl alcohol, polyacrylic acid, polyethylene glycol, polypropylene glycol, polyfunctional polyols, N,N,N',N'-tetrakis (2-hydroxypropyl)ethylenediamine and polycaprolactone polyol. Hydrophobic polymers include polyether or polyester polyols, block copolymers of ethylene and propylene oxides on a propylene glycol base, the block copolymers being useful as components in any proportion so long as the resulting block copolymer is hydrophobic. The preferred materials should have two or more reactive hydroxy sites per chain for reaction with the crosslinking agent.

The molecular weight of such materials is not overly important since they will be at least partially crosslinked; however, prior to crosslinking, typically they will exhibit a molecular weight on the order of about 100 to about 2,000 (all molecular weights herein are number average molecular weight).

Crosslinking can be by any conventional means to crosslink the particular polymer involved, e.g., by chemical crosslinking, by thermal crosslinking, by high energy particle crosslinking, combinations thereof, or the like.

The following are representative examples of various crosslinked polymer systems for application according to this invention:

Urethane crosslinked coatings are based on aliphatic polyisocyanates, typically in the presence of suitable dispersing agents, catalysts and wetting agents well known to those skilled in the polyurethane art. Typical polyisocyanates that react with available -OH groups of the hydrophilic polymer include hexamethylene diisocyanate-based systems such as Desmodur N-75 (aliphatic prepolymer, Mobay Chemical Co.) Aromatic polyisocyanates are generally not used as crosslinking agents. Melamine crosslinking agents can also be employed to obtain thermoset coatings with hydroxy group carrying binders. The conductive solid lubricant and scouring agent can be incorporated by the usual techniques of grinding or milling together with the binder, a urethane solvent such as an MEK-toluene mixture, and a suitable dispersing agent such as Multron R221-75, a saturated polyester resin by Mobay Chemicals.

The isocyanate compounds used in the binder typically have a molecular weight of 150-500 per NCO group. The polyisocyanates have at least three reactive sites, i.e., NCO groups, per chain so that crosslinking and thermosetting properties are established in the resulting binder.

The cross linking reaction can be accelerated using conventional catalysts as are known in the art. Useful catalysts are disclosed in European Application 113005. Catalyst concentrations of about 0.1 to about 1.5 percent by weight based on total organics are usually satisfactory. Further acceleration can be achieved by thermal treatment.

Desired crosslinked films can also be formed by thermal, microwave, or UV curing of coatings cast from blends of hydrophilic polymers and UV curable crosslinking agents.

It is most preferred that about 0.1 to about 0.5 weight part of a crosslinker such as a polyisocyanate, etc., be used per 1 weight part of the binder. Some hydrophilic or hydrophobic sites should remain after crosslinking, of course.

There exists a latitude in useful overlayer formulations without significantly affecting the functional characteristics of the overlayer. For example, the NCO:OH ratio can be varied from 0.1 to 0.5 and dry overlayer density between about 1.0 to about 20 micrograms/cm^2. The conductive solid lubricant to binder ratio can vary from about 80:20 to about 50:50 by weight, the scouring agent can range from about 2 to about 10% of the weight of the solid conductive lubricant, and the catalyst concentration preferably ranges between 0.5-1.5 wt.% based on binder and crosslinker weight for crosslinking during the curing.

Drying/curing is usually at about 100°C ± 15°C for about 1 to about 10 minutes. Higher and lower temperatures and times can be used, if desired.

For catalyzed polyisocyanate systems, crosslinking is typically at an elevated temperature of about 100°C, sufficient crosslinking being easily effected in a time of from about 5 minutes to about 10 minutes in air at these conditions to provide tack-free, hard, adherent and abrasion-resistant films.

The use of a catalyst reduces the curing temperature and curing time. Minimum curing temperature and shortened cure time are desirable to limit any adverse effects on the substrate, such as, distortion of a polymer substrate, e.g., Mylar ®.

Conventional dispersing agents and surfactants can be used. if desired.

Several types of volatile non-reactive solvents can be used in the production of the compositions of the invention to reduce the solids content and permit the coating of very thin overlayers. Classes of suitable solvents include, but are not limited to, aromatic solvents, such as, toluene and xylene; ketones, such as, methyl ethyl ketone and isophorone; acetates, such as ethyl acetate and butyl acetate; and alcohols such as isopropyl alcohol. The preferred solvents employed in the overlayer composition are isopropanol, tetrahydrofuran or a mixed solvent such as 80 parts by weight of methyl ethyl ketone and 20 parts by weight of toluene or THF-toluene mixtures. While not to be construed as limitative, we have found that an amount of solvent sufficient to provide 5 to 10 wt % total solids (lubricant, binder, and crosslinker), balance solvent, are quite acceptable.

In general the overcoat layer should have a dry density between about 1.0 and about 20 micrograms/cm^2, since lower thicknesses give inadequate lubrication and higher thicknesses are detrimental to good writing at low writing voltages (about 50 V) and short pulse lengths (about 3 microseconds). If more energy is applied by increasing the voltage of the writing pulse and increasing the pulse length, thicker films can be used. Also the lubricating agent-binder ratio should be adjusted to avoid flake off of the lubricating agent and the scouring agent when employed.

The Conductive Solid Lubricant

The conductive solid lubricant is not limited per the present invention so long as it is a conductive particulate solid.

The general class of laminar solids may be employed as such conducting agents. Examples of such solids are graphite, carbon black, MoS_2, WS_2, TaS_2 and graphite. Other compounds may be considered such as ZnO, TiO_2 and CaF_2 since they have all been shown to be lubricants and conductive. In addition, soft metal particles such as Sn, Cu, Zn, Ag, Pb, Au, Bi and Al are expected to be useful in the invention. Work has been carried out with MoS_2, Al, and Zn, but graphite was found to be most satisfactory in terms of its effectiveness as a conductive lubricant and dispersability and coating quality.

A variety of suitable graphite compositions have been found to be available commercially as ELECTRO-DAG 154 from Acheson Colloid Co., colloidal graphite suspensions from Superior Graphite Co. and from Graphite Products Corp. or Superior Graphite Corp.; ELECTRO-DAG 154 comprises graphite dispersed in a cellulose derivative such as ethyl cellulose and isopropanol as a solvent (about 20 wt % solids, 20 wt % of which is binder and 80 wt % of which is graphite), balance solvent. After the coating is applied, only a short drying cycle (about 3 minutes at 100°C) is needed to drive off the solvent. Colloidal Suspension No. 150 from Superior Graphite Co. contains purified carbon/graphite of an average particle size less than one micron in water while No. 211 is a similar suspension in trichloroethane. Dag 191 is an aqueous dispersion of graphite in a hydrophilic binder which has 15% total solids of which 90% is graphite and the balance is binder and surfactant.

It is found that a wide range of binder concentrations can be effectively used, e.g., from about 10% binder to 90% conductive agent/scouring agent, to from about 60% binder to 40% conductive agent/scouring agent. The change in binder concentration changes the electrical conductivity of the overlayer. Depending on the details of the driver circuitry of the electroerosion printing system, in particular the maximum initial current which can be delivered by the drivers, it may be advantageous to employ a higher binder content so long as it does not interfere with the printing quality due to possible fouling caused by polymer debris sticking to the print head during writing.

Optimum concentration of organic components in the crosslinked overlayer that has been found to be most satisfactory to provide the desired resistance to smudging and flake off during handling, wear resistance and print quality has been found to be 25-35% by weight, although binder contents of 20-50% by weight have total solids in layer, based on total solids in the layer, also been employed without adversely affecting print quality.

Size is not overly limited, but normally the particulate conductive agent will have a size of from about 0.1 to about 2.5 microns.

When graphite is used as the conductive agent, it most preferably has a size of less than 1 micron.

The solid conductive lubricant such as graphite in these overlayers imparts lubricity, increased contrast between written and unwritten areas, electrical conductivity and helps suppress electrode fouling, while the crosslinked polymer provides a coherent, wear-resistant matrix. The optional scouring agent further provides protection against fouling. Such an overlayer, when hydrophilic and water-resistant, provides an ink-repelling background similar to aluminum in terms of wetting characteristics but is superior in terms of wear life on the press during the printing operation. Typically, this overlayer will be on the order of about 2.0 to 35 micrograms per square centemeter in dry density, and long press life for the direct master will be insured.

The Scouring Agent

The purpose of the scouring agent, which is also a particulate solid, is basically to remove organic/inorganic residue which might adhere to the electrodes during electroerosion recording.

Accordingly, most preferably the scouring agent will be a hard particulate material, for example, a material exhibiting a MOH's hardness of at least about 6, though preferably no greater than about 9 such as silica, alumina, titania, ZnO, etc.

The scouring agent can be relatively freely selected from materials which do not degrade the at least partially crosslinked polymer or interact with the particulate conductive solid. Useful materials can be selected from metal oxides of Group III and Group IV elements (see the Chemical and Physics Handbook, CRC Press, ed. by Robert C. Weast).

The particle size thereof is not particularly limited so long as the desired scouring function is exhibited, but most preferably, with electroerosion electrodes as are currently in use, the particle size of the scouring particles will be on the order of from about 0.1 to about 3 microns.

Layer Formation

The layers are formed using conventional techniques as earlier discussed.

The overlayer comprising a conductive lubricant solid and the crosslinked polymer is typically formed by blending the non-crosslinked polymer, the conductive lubricant and the optional scouring particles in an appropriate solvent using a conventional ball milling technique. The resulting homogenous dispersion is thoroughly mixed with a crosslinking agent followed by appropriate dilution and application on the metallized substrate.

Following application of the components of the overlayer, typically a dry/cure cycle is conducted, whereafter the overlayer is at least partially cured at the desired conditions as earlier described.

Having thus generally described the invention, the following working examples are offered to further illustrate the invention. Unless otherwise indicated, all parts are by weight.

EXAMPLE 1

Fabrication of a typical structure consisted of a transparent polyester substrate, specifically a 50 μm thick Mylar ® sheet on which a 5-7 μm thick hard underlayer comprised of a silica pigmented urethane crosslinked cellulosic binder had been coated and dried/cured, as disclosed in Example 1 of EP-A-113005.

On the above underlayer an aluminum film 300-500 nm thick was deposited by vacuum evaporation in a conventional manner.

A protective overlayer comprised of graphite and a hydrophilic polymer matrix which is to be crosslinked per the present invention was formed as described below.

The following ingredients were combined in ball milled to form a homogenous dispersion where all parts are parts by weight:

	Parts by Weight
Polytetramethylene Ether Glycol ..... (Teracol 1,000 available from Dupont; molecular weight=1,000, per vendor)	1.0
Tetrahydrofuran .... (THF)	5.0
Colloidal graphite No. 211 .... (Superior Graphite Co.)	10.0
Hydroquinone .... di(beta-hydroxyethyl) ether	0.2
Trimethylol propane	0.05
Irganox 1010	0.005

Prior to coating application, the dispersion was combined with 0.5 part of a polyisocyanate (Desmodur N-75 from Mobay Chemical Co.) dissolved in 5 parts of a 3:2 volume mixture of THF-toluene, mixed thoroughly and applied on the aluminum layer using a conventional web coating apparatus followed by drying/curing at about 100°C for 5∿10 minutes to obtain a dry coating thickness of 10 to 15 micrograms per cm^2. The overcoat was removed prior to use as a direct master with an oleophilic inks.

EXAMPLE 2

The procedure of EXAMPLE 1 was followed except that a modified overlayer was formed by including 0.5 part of zinc oxide (New Jersey Zinc Co.) among the ingredients recited in EXAMPLE 1 before ball milling. The final coating formulation containing the polyisocyanate crosslinking agent was prepared following the procedure of EXAMPLE 1 and applied onto the aluminum surface to form a protective layer having a dry density of 10 to 20 micrograms per cm^2.

Other polyether and polyester glycols that can be substituted for the Teracol 1,000 of EXAMPLE 1 and 2 are: Teracol 2,000, polycaprolactone glycol, polyethylene adipate glycol, polypropylene ether glycol and similar polyols.

For the overlayer according to the present invention it is preferred that the isocyanate crosslinking agents be a mixture of di-functional and tri-functional isocyanates or a polyisocyanate with more than two-N=C=O functional groups as crosslinking sites such as MDI, "Papi" 901 (Upjohn Chemicals), Desmodur N-75 (Mobay Chemical Co.), Mondur CB60 (Mobay Chemical Co.), Isocyanurate T1890 and similar materials.

EXAMPLE 3

The procedure of EXAMPLE 1 was followed except that the overlayer was formed from a homogeneous dispersion of the components below where all parts are by weight.

	Parts by Weight
Acrylic acid-Acrylamide copolymer* ...	1.0
Methyl ethyl ketone (MEK)	6.0
Toluene	4.0
Colloidal Graphite No. 211 .... (Superior Graphite Co.)	10.0

Dispersing agent .... (Mondur R221-75)	0.05

* Molecular weight from 20,000∿80,000; 65:35 molar.

The mixture was ball milled to form a uniform dispersion to which was added a solution of a polyisocyanate crosslinking agent (Desmodur N-75; 0.5 part in 5.0 parts of MEK-toluene mixture, 3:2 by volume), 0.01 part of T-9 catalyst (stannous octoate; M T Co.) and 0.02 part FC-430 (3M Co.).

The mixture was thoroughly shaken in a paint shaker for 5-10 minutes and applied to provide and dried/cured to provide an overcoat, following the procedure of EXAMPLE 1.

EXAMPLE 4

Following the procedure of EXAMPLE 3, the overcoat composition described in EXAMPLE 3 was modified by adding ZnO, TiO_2 or silica particulate material prior to ball milling. Subsequent processing and application following the procedure of EXAMPLE 3 provides overlayers which exhibit further protection against fouling during electroerosion printing.

EXAMPLE 5

Following the procedure of EXAMPLE 1, a homogeneous dispersion of the following components was prepared for overcoat formation. Unless otherwise indicated, all procedures were per EXAMPLE 1 and all parts are parts by weight.

	Parts by Weight
Polyvinyl alcohol (avg. mol. wt. 2,000)	1.0
Colloidal graphite suspension (Aqua Dag, 0.02 nm mean diameter; Acheson Chemical Co.)	5.0
Aluminum oxide (1-2 nm mean diameter)	0.2
Polyol, Pluronic L62	0.1
Water	20.0

The mixture was ball milled for 16 hours, combined with methylol melamine (0.2 parts) and the pH was adjusted to 5~5.5 in a conventional manner.

The formulation was thoroughly mixed and applied on the aluminized substrate and dried/cured all as per EXAMPLE 1 to provide the desired water-based protective overlayer. Other molecular weight polyvinyl alcohols can be used, of course, e.g., of a molecular weight of 20,000~50,000.

EXAMPLE 6

The procedure of EXAMPLE 3 was followed except that the overlayer was formed from a homogeneous dispersion of the components below where all parts are by weight.

	Parts By Weight
CAB*	1.0
MEK	6.0
Toluene	4.0
ELECTRO-DAG 154	10.0

* unless otherwise indicated, the CAB was CAB 553.4 available from Eastman Kodak; viscosity: 405 cps as a 15 wt % solution in isopropanol (Brookfield Viscometer).

Processing per EXAMPLE 3 provided a cross-linked hydrophobic overlayer having a dry coating thickness of 0.4 to 0.6 microns. For direct master use, after electroerosion remaining overlayer in unwritten layers is removed with a conventional cleaning solution or with isopropanol, trichloroethane or MEK by swabbing.

EXAMPLE 7

Unless otherwise indicated, all layers, process conditions, etc., were per EXAMPLE 1. The protective overlayer was formed from the following composition. All parts and percents are by weight.

	Parts by Weight
5% aqueous solution of a styrene-maleic anhydride copolymer* (ammonium salt); Scripset® 720 from Monsanto	2.0
Dag 191 (graphite dispersion in water)	4.0

* Molecular wt. ca. 50,000 avg.; 50:50~25.75 molar ratio (approx.); Vendor supplied as a 25% aqueous solution, diluted to 5% with water.

The above components were stirred for five minutes at high shear, web coated on the conductive film and dry/cured at 120°C for 1~5 minutes in air to provide a dry thickness of ca. 5 micrograms/cm^2 (usually 2~20 micrograms/cm^2 provides good results).

The resulting protective overlayer had a contact angle with water of ca. 30° and was highly adherent to the conductive film.

After electroerosion it provided a scratch-free direct negative. For direct master use it is preferably removed in a conventional printing press cleaning solution. Even after what appeared to be complete removal of the protective overlayer the resulting direct master provided two or more times as many copies as an otherwise similar direct master where no protective overlayer had been formed. We are unsure as to the reason(s) for this unexpected result.

When employed as printing material using an electroerosion device at 30-60 volts the material thus formed may be imaged by clean erosion of aluminum which is accompanied by the removal of the overlayer in the written or imaged areas thereby exposing the base coat when used with consequent generation of the scratch-free direct negative and direct offset master since the overlayer in the unwritten areas is non-receptive to oil based or aqueous inks, depending on if it is hydrophobic or hydrophilic inks.

For application of such a printed or imaged material as an offset master, the written area may remain ink receptive while the unwritten area may be non-receptive to oil based inks depending upon the composition of the oil-based ink used.

While there have been described what are at present considered to be the preferred embodiments of this invention, it will be obvious to those skilled in the art that various changes and modifications can be made therein without departing from the invention, and it is, therefore, intended to cover all such changes and modifications as fall within the true spirit and scope of the invention.

CLAIMS;

1. In a method of making a direct negative or direct offset master by electroerosion, the improvement wherein an electroerodable conductive layer on a support is overcoated with a crosslinked polymer containing a solid conductive lubricant, whereafter the conductive layer is selectively electroeroded, thereby selectively simultaneously removing the crosslinked polymer layer.

2. The method of Claim 1, wnerein the crosslinked polymer is hydrophilic.

3. The method of Claim 1, wherein there is further present between said support and said electroerodible conductive layer a hard polymeric base layer.

4. The method of Claim 1, wherein the overcoat of the crosslinked polymer contains conductive particles and scouring particles and is coated so as to have a dry density between about 1 and about 20 micrograms per square centimeter.

5. The method of Claim 2, wherein said hydrophilic polymer is selected from the group consisting of polyvinyl alcohol, polyethylene glycol, polypropylene glycol and polycaprolactone polyol.

6. The method of Claim 1, wherein said crosslinked polymer is crosslinked to a degree of from about 10 to about 50%.

7. The method of Claim 1, wherein said solid conductive lubricant is graphite having a particle size of about 0.1 to about 2.5 microns.

8. The method of Claim 4, wherein said scouring particles are selected from the group consisting of silicon dioxide and aluminum oxide having a particle size of about 0.1 to about 3.0 microns.

9. The method of Claim 2, wherein said crosslinked hydrophilic polymer is crosslinked using an aliphatic polyisocyanate having at least three isocyanate groups per molecule.

10. The method of Claim 2, wherein said crosslinked hydrophilic polymer containing conductive particles and scouring particles and has a dry thickness of about 1 to about 20 micrograms per square centimeter, the hydrophilic polymer is selected from the group consisting of polyvinyl alcohol, polyethylene glycol, polypropylene glycol and polycaprolactone polyol and crosslinking is to a degree of about 10 to about 50%, the conductive particles are graphite having a size of about 0.1 to 2.5 microns, the conductive particles are selected from the group consisting of silicon dioxide and aluminum oxide having a particle size of about 0.1 to about 3.0 microns and

crosslinking is with an aliphatic polyisocyanate having a least three isocyanate groups per molecule.

FIG. 1

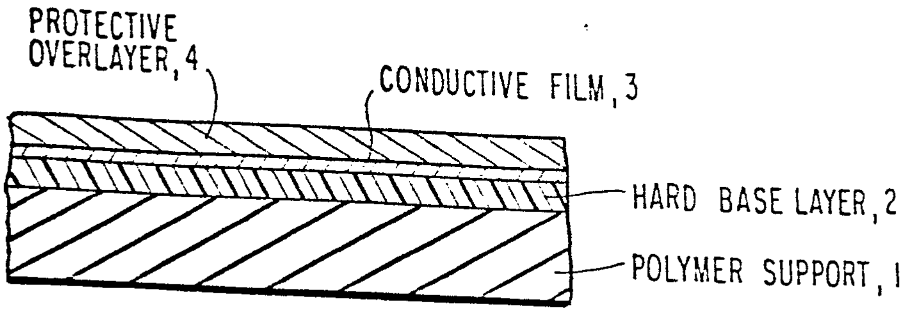
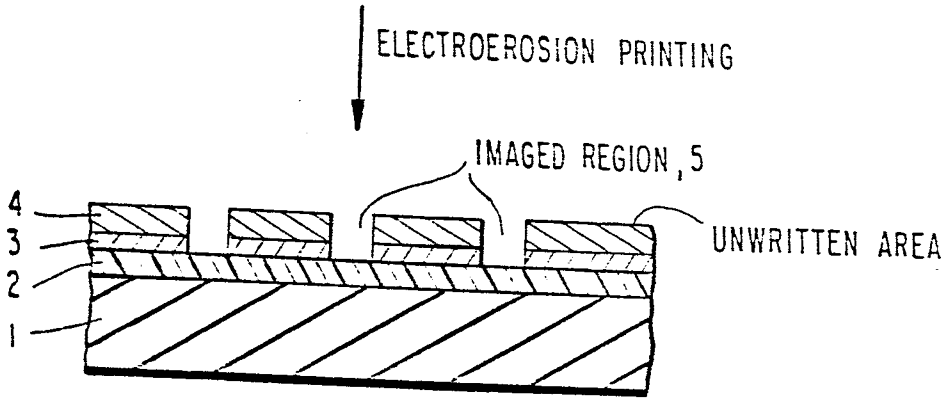
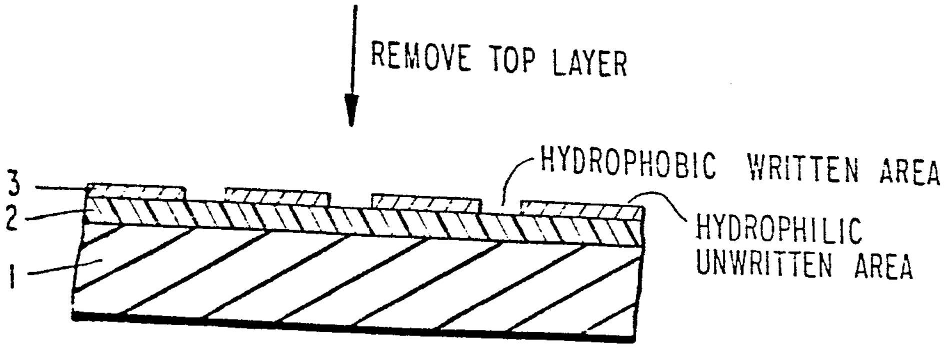


FIG. 2



DIRECT NEGATIVE

FIG. 3



DIRECT OFFSET MASTER