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[54] **SULFONATED PLASTIC DUPLICATING MASTERS**

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[58] **Field of Search**.....101/470, 471, 473, 467, 457, 101/462, 453, 465; 117/118, 47 A; 250/65 T; 264/80, 232, 340

[56] **References Cited**

UNITED STATES PATENTS

2,304,541	8/1942	Caton	101/462
2,808,777	10/1957	Roshkind	101/471 X
3,035,916	5/1962	Heiart	117/47 A X
3,256,811	6/1966	Bach	101/467
3,418,935	12/1968	Adams	101/348
3,455,003	7/1969	Wood	101/147 X
3,532,532	10/1970	Berman	101/470 X

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[57] **ABSTRACT**

Plastic duplicating masters comprising a film of sulfonated plastic on which is fused an imaged coating of a duplicating composition such as a lithographic or hectographic composition. The imaged coating is obtained by exposing a composite of an original document, a transfer sheet having a fusible duplicating coating, and the sulfonated film to visible radiation, infrared radiation, or a combination of these for a short time.

10 Claims, No Drawings

SULFONATED PLASTIC DUPLICATING MASTERS

BACKGROUND OF THE INVENTION

This invention relates to duplicating masters which are useful in the lithographic and hectographic manifolding field of use.

It is known from U.S. Pat. No. 2,808,777 that an imaged duplicating master can be prepared on a water receptive substrate by fusing or melting onto the substrate an hydrophobic material in areas corresponding to an original document. These lithographic masters are commonly made from sheets of cellulose acetate film with a layer of absorbtive clay bound to the surface thereof with a binder composition. These known lithographic masters are relatively expensive and difficult to make because of the coating steps involved and the difficulty in obtaining good adhesion between the clay coating and the substrate.

SUMMARY OF THE INVENTION

It now has been found that duplicating masters can be made from sulfonated plastic films in an economic manner which effectively overcomes the disadvantages of the prior art and which are substantially equal to the prior duplicating masters from a printing standpoint.

In accordance with this invention, there is provided a duplicating master comprising a sulfonatable plastic base and a surface thereon comprising a sulfonated layer of said plastic having a plurality of sulfonic groups and a duplicating imaged coating thereon. There is also provided a composite useful to make the duplication master comprising a sulfonated plastic sheet and a transfer sheet having a duplicating coating thereon. The sulfonic groups can be either sulfonic acid groups or sulfonic acid salts groups. The sulfonic acid salt groups can be salts wherein the cationic moiety is ammonium, substituted ammonium, or metal ions.

The duplicating coating can be either an easily melted lithographic composition or an easily melted, colored, non-infra-red absorbing, hectographic composition.

The duplicating master is made by a process in which an original document is placed above or below a composite comprising a transfer sheet coated with a duplicating fusible coating and the surface sulfonated plastic base in which the sulfonated surface of the plastic base is in direct contact with the fusible coating of the transfer sheet. The formed composite is then irradiated with sufficient visible light, infra-red rays, or a combination of these to generate heat in the imaged portions of the original which is conducted to the coated transfer sheet and causes the coating thereon to melt and transfer to the sulfonated master sheet in areas corresponding to the imaged original to form a reversed image on the master sheet.

DETAILED DESCRIPTION

The duplicating masters of this invention are made from sulfonatable plastic sheets, films, or laminates of a thickness in the range from about 1 to about 50 mils and of a size which can be varied to suit the requirements of the particular duplicating machine on which they are used. Examples of these duplicating machines are off-set lithographic printing machines as exemplified by the Addressograph Off-Set press and the hectographic printing machines as exemplified by the Ditto machines.

Examples of suitable sulfonatable plastics which can be used as bases to form the duplicating masters are polyolefins such as polyethylene, polypropylene, polymethylpentene, and polybutene; polyamides such as nylon; polyesters such as polyethylene terephthalate; polyvinyl chloride; polyvinyl acetate; polyvinylidene chloride; polyacrylates; styrene polymers; polycarbonates; polyethers such as polyacetals; cellulose esters, and cellulose ethers. Also included within the scope of the term sulfonatable plastics are copolymers made from monomers of the above synthetic polymers as well as blends and mixtures of the above polymers. Laminates of the above polymers, copolymers, and blends are also included within the scope of the term sulfonatable plastics. Laminates are used whenever it is desired to obtain a combination of properties or to use a relatively expensive plastic in a thin layer laminated to a cheaper base material. Examples of these are: polyvinylidene chloride laminated to one or both sides of a sheet of polyethylene and polyethylene terephthalate laminated to one or both sides of a sheet of polystyrene.

The above plastic sheets are preferably biaxially oriented for greater strength.

Biaxially oriented styrene polymers are particularly preferred because of their low cost and strength.

Typical examples of oriented styrene polymer films and sheets are unmodified polystyrene, high impact polystyrene blends, and high impact styrene copolymer blends.

In general, the high impact polystyrene blends comprise a blend of a minor amount of synthetic rubber with polystyrene. The amount of synthetic rubber used is in the range of 1–6 percent by weight while the preferred range is 2–3 percent by weight based on the weight of the polystyrene. Examples of typical impact modifying synthetic rubbers are styrene-butadiende copolymers, acrylonitrile-butadiene copolymers, polyisoprene, polybutadiene, isobutylene-butadiene copolymers, isobutylene-isoprene copolymers and the like.

A minor amount of rubber impact modifiers ranging from about 1–6 percent by weight can be copolymerized with aromatic monomers and monomers of the group consisting of methacrylic acid esters, itaconic acid esters, and acrylonitrile to produce films when oriented having good transparency provided that the synthetic rubber used has a refractive index in the range from n_D^{25} 1.513 to 1.576.

Examples of these known interpolymers are styrene/methyl methacrylate/styrene-butadiene copolymers; styrene/acrylonitrile/styrene-butadiene copolymer; styrene/dimethylitaconate/styrene-butadiene copolymer and the like.

In accordance with the present invention, the above polymer films, sheets or laminates are sulfonated, preferably, with sulfur trioxide gas in a pure or dilute form, to produce films having a plurality of sulfonic acid groups directly attached to the polymer on the surface of the article.

It is preferred to sulfonate the sheets on one side only by moving them through a blast or curtain of sulfur trioxide gas in the absence of water or water vapor as

this technique provides a method with great speed, uniformity, and no complications such as removal of solvents, etc. The sheets can be sulfonated on both sides if desired but only one side is needed or used herein. Alternatively, the sheets are passed through a static or quiescent atmosphere of gaseous sulfur trioxide. In this technique, slower speeds may be necessary to give adequate contact time between the sheet and the gas.

The sulfur trioxide gas can be used pure but since sulfur trioxide boils at 44.8° C it is difficult to keep in the vapor state. The preferred method is to dilute vapors of sulfur trioxide with a dry inert gas such as air, carbon dioxide, nitrogen, and the like. A range of concentration of the SO_3 in the inert gas can be from 1–15 percent.

Another method of sulfonating the polymer films is to treat them with a solution of SO_3 dissolved in an inert liquid solvent. The solvent is then removed and the sheet washed. Typical useful inert liquid solvents are hydrocarbon solvents such as hexane, heptane, petroleum ether, kerosene, etc.

The range of concentration of SO_3 in the above solvents can be from 1–25 percent by weight SO_3 but it is preferred to use a lower range of from 1–5 percent by weight SO_3.

In the foregoing sulfonation processes the temperature can range from −20° to 60° C with the preferred temperature range being 20° to 40° C.

The pressure at which the sulfonation is carried out can be atmospheric or superatmospheric. Because of the convenience, it is preferred to carry out the sulfonation at atmospheric pressure. However, the reaction can also be carried out at a pressure of 1–10 pounds per square inch gauge.

For the purposes of this invention, a plurality of sulfonic groups is defined as that amount which is equivalent to about 0.0001 to about 5.0 milligram sulfur trioxide per square centimeter. The sulfonic groups can be either sulfonic acid groups or sulfonic acid salt groups wherein the cationic moiety is ammonium, substituted ammonium, or metal ions. Examples are ions of the light metals of Groups IA and IIA of the Periodic chart such as sodium, potassium, calcium, lithium, rubidium, cesium, magnesium, barium, strontium and the heavy metals of Groups VB, VIB, VIIB, VIII, such as copper, zinc, vanadium, chromium, manganese, and iron. These metals are used in the form of their water soluble salts.

Examples of water soluble amines which can be used to form substituted ammonium sulfonic acid salt groups are ethanolamine, diethanolamine, triethanolamine, and the like.

The sulfonic acid salt groups are obtained on the polymer sheets by dipping, wiping, or spraying the sulfonated sheets in or with an aqueous solution of the appropriate water soluble metal salt, water soluble amine, or an aqueous ammonia solution, then washed and dried. If desired, the sulfonated sheets can also be treated with gaseous ammonia.

The foregoing sulfonated plastic sheets, films, or laminates are then converted into duplicating masters by assembling them into a composite with an original document which is to be reproduced, and a transfer sheet having on its surface a fusible duplicating coating so that the coating of the transfer sheet is in contact with the sulfonated surface. The composite is placed under a source of light rays rich in infra-red radiation such as a commercially available thermographic copying apparatus, e.g., "Thermofax" and irradiated. The imaged portions of the original document receive and absorb the infrared rays and the heat generated is conducted to the coated transfer sheet where the fusible coating melts and transfers to the sulfonated surface of the plastic sheet to form a duplicating master imaged with the fusible coating in areas corresponding to the original document.

It is preferred to use transparent plastic sheets or films for the master sheet since then the light and/or infra-red radiation can pass through the transfer sheet and the master sheet before contacting and heating the imaged areas of the original document. However, translucent or opaque master sheets can be used provided that the light and/or infra-red radiation strikes the imaged original document first and heats the underlying transfer sheet and master sheet. It is, of course, always essential that the coated side of the transfer sheet be in contact with a sulfonated surface of the master so that a reverse image of the original is formed on the master sheet.

The composite can also consist of additional sheets such as interleaver sheets and a cover sheet to protect the composite during storage and shipment. Obviously, these additional sheets are removed just prior to the use of the composite in the thermographic copier.

In the preparation of a duplicating master for lithographic purposes, the transfer sheet must be coated with an ink receptive fusible composition. These compositions are well known and are usually waxes, fatty acids, fatty oils, chlorinated hydrocarbons or blends of these. Examples of these are carnauba wax, ceresin wax, parafin wax, stearic acid, tallow acids, and chlorinated naphthalenes and blends thereof.

In the preparation of a duplicating master for hectographic purposes, the transfer sheet must be coated with a fusible composition containing a spirit-soluble, non-infrared absorbing dye. These compositions are well known and typically consist of a blend of carnauba wax, lanolin, mineral oil, and a dye such as rhodamine, malachite green, safranine, and other non-infrared absorbing dyes.

The following examples are presented solely to illustrate the invention and are not to be considered a limitation therein.

EXAMPLES 1–9

Several samples of biaxially oriented, 1½ mil, polystyrene film were sulfonated on one side by moving them through apparatus which provides a curtain or blast of 2 percent sulfur trioxide gas in carbon dioxide. Some of these sulfonated films were subsequently neutralized with a blast of gaseous ammonia. Some of these sulfonated films were subsequently dipped into aqueous solutions of 1 percent by weight of sodium hydroxide, 2 percent by weight of potassium hydroxide and 3 percent by weight of calcium chloride respectively.

The above treated films after being washed and dried were then assembled into composites with a document to be copied, and a commercially available transfer

sheet having a fusible coating of an ink receptive wax, i.e., an "offset carbon" from the Columbia Carbon and Ribbon Company.

The original document was placed on the bottom of each composite with the sulfonated and/or neutralized polystyrene sheet placed on top of this and the transfer sheet uppermost with the coated side in contact with the sulfonated surface of the polystyrene sheet. The composites were then placed in a Thermofax copier and irradiated with light through the transfer sheet for two seconds.

After the composite was disassembled, the imaged master sheet was placed in a commercial offset duplicating machine (Addressograph) and copies were run off the machine until the master wore out. The following table gives the results.

TABLE I

Example	Speed of Sulfonation (ft/min.)	Cation	Copies
control (not sulfonated)	0	0	0
1	12*	H^+ (sulfonated only)	125
2	40**	do	150
3	50***	do	125
4	12	NH_4^+ (sulfonated & neutralized with ammonia)	50
5	40	do	125
6	50	do	100
7	12	Na^+	175
8	40	K^+	125
9	50	Ca^+	50

*Corresponds to .001 mg/cm² of SO_3 equivalents.

**Corresponds to .0005 mg/cm² of SO_3 equivalents.

***Corresponds to .0004 mg/cm² of SO_3 equivalents.

The foregoing data indicate that sulfonated platic films can be used as an effective replacement for the known clay coated masters which give runs of about 200 copies under similar conditions.

Similar efficacious results are obtained with the other sulfonated polymers mentioned above.

Following the procedures of examples 1–9, hectographic duplicating masters are prepared by using a transfer sheet having a fusible coating of a spirit soluble blend of waxes, oils, and a non-infrared adsorbing dye.

We claim:

1. A duplicating master having a coating thereon corresponding to the characters of an original document comprising a sulfonatable polymer base, a water receptive surface thereon comprising the polymer having a plurality of sulfonic acid groups attached thereto in an amount of from about 0.0001 to about 5 milligrams sulfur trioxide equivalents per square centimeter, and a patterned coating of a fusible, hydrophobic composition on said surface.

2. A duplicating master having a coating thereon corresponding to the characters of an original document comprising a sulfonatable polymer base, a water receptive surface thereon comprising the polymer having a plurality of sulfonic acid groups attached thereto in an amount of from about 0.0001 to about 5 milligrams sulfur trioxide equivalents per square centimeter in which said sulfonic acid groups are treated with water-soluble metal salt, water-soluble amine, aqueous ammonia solution or gaseous ammonia to form sulfonic acid salt groups, and a patterned coating of a fusible, hydrophobic composition on said surface.

3. A duplicating master as set forth in claim 2 in which said sulfonic acid groups are treated with aqueous ammonia solution or gaseous ammonia.

4. A duplicating master as set forth in claim 2 in which said sulfonic acid groups are treated with water-soluble salts of the light metals of Group IA and IIA of the Periodic Chart.

5. A duplicating master having a coating thereon corresponding to the characters of an original document comprising a sulfonatable polymer base, a surface thereon comprising the polymer having a plurality of sulfonic acid groups attached thereto in an amount of from about 0.0001 to about 5 milligrams sulfur trioxide equivalents per square centimeter and patterned coating of a fusible hectographic composition on said surface.

6. A duplicating master having a coating thereon corresponding to the characters of an original document comprising a sulfonatable polymer base, a surface thereon comprising the polymer having a plurality of sulfonic acid groups attached thereto in an amount of from about 0.0001 to about 5 milligrams sulfur trioxide equivalents per square centimeter in which said sulfonic acid groups are treated with water-soluble metal salt, water-soluble amine, aqueous ammonia solution or gaseous ammonia to form sulfonic acid salt groups, and a patterned coating of a fusible hectographic composition on said surface.

7. A process for making an imaged duplicating master from an original document having imaged portions, a surface sulfonated plastic master sheet having a water receptive surface containing a plurality of sulfonic acid groups in an amount of from about 0.0001 to about 5 milligrams of sulfur trioxide equivalents per square centimeter and a transfer sheet coated with a fusible, hydrophobic composition which comprises:

1. placing the original, the surface sulfonated master and transfer sheet coated with the fusible composition in contact with each other, so that the sulfonated surface of the master is in direct contact with the fusible composition of the transfer sheet, and
2. irradiating the original with sufficient light rays to generate heat in the imaged portions of the original document, which heat is then conducted to the coated transfer sheet and which causes the coating to melt and transfer to the sulfonated master sheet in the areas corresponding to the imaged portions of the original document.

8. The process as set forth in claim 7 wherein the master sheet has, prior to placing it in contact with the original and the transfer sheet, been treated with water-soluble metal salt, water-soluble amine, aqueous ammonia solution or gaseous ammonia to form sulfonic acid salt groups.

9. A process for making an imaged duplicating master from an original document having imaged potions, a surface sulfonated plastic master sheet having a surface containing a plurality of sulfonic acid groups in

an amount of from about 0.0001 to about 5 milligrams of sulfur trioxide equivalents per square centimeter and a transfer sheet coated with a fusible hectographic composition which comprises:

1. placing the original, the surface sulfonated master and transfer sheet coated with the fusible composition in contact with each other, so that the sulfonated surface of the master is in direct contact with the fusible composition of the transfer sheet, and
2. irradiating the original with sufficient light rays to generate heat in the imaged portions of the original document, which heat is then conducted to the coated transfer sheet and which causes the coating to melt and transfer to the sulfonated master sheet in the areas corresponding to the imaged portions of the original document.

10. The process according to claim **9** wherein the master sheet has, prior to placing it in contact with the original and the transfer sheet, been treated with water-soluble metal salt, water-soluble amine, aqueous ammonia solution or gaseous ammonia to form sulfonic acid salt groups.

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